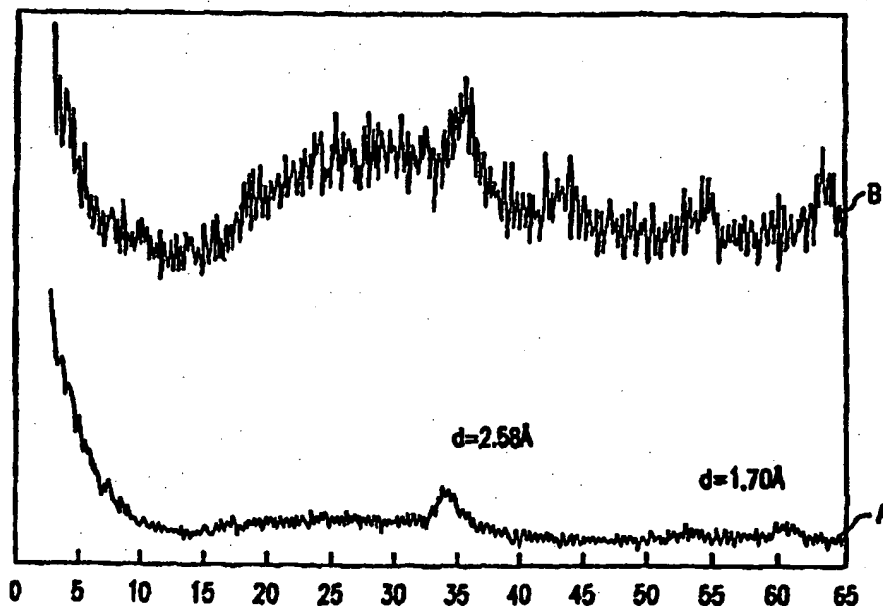


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(54) Title: HYDROPROCESSING USING BULK GROUP VIII/GROUP VIB CATALYSTS



(57) Abstract

Hydroprocessing of petroleum and chemical feedstocks using bulk Group VIII/Group VIB catalysts. Preferred catalysts include those comprised of Ni-Mo-W.

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HYDROPROCESSING USING BULK GROUP VIII/GROUP VIB CATALYSTS

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Ser. No. 09/231,156 filed January 15, 1999 which is a continuation-in-part of U.S. Ser. No. 08/900,389 filed July 15, 1997.

FIELD OF THE INVENTION

This invention relates to the hydroprocessing of petroleum and chemical feedstocks using bulk Group VIII/Group VIB catalysts. Preferred catalysts include those comprised of Ni-Mo-W.

BACKGROUND OF THE INVENTION

As the supply of low sulfur, low nitrogen crudes decrease, refineries are processing crudes with greater sulfur and nitrogen contents at the same time that environmental regulations are mandating lower levels of these heteroatoms in products. Consequently, a need exists for increasingly efficient desulfurization and denitrogenation catalysts.

In one approach, a family of compounds, related to hydrotalcites, e.g., ammonium nickel molybdates, has been prepared. Whereas X-ray diffraction analysis has shown that hydrotalcites are composed of layered phases with positively charged sheets and exchangeable anions located in the galleries between the sheets, the related ammonium nickel molybdate phase has molybdate anions in interlayer galleries bonded to nickel oxyhydroxide sheets. See, for example, Levin, D., Soled, S. L., and Ying, J. Y., Crystal Structure of an Ammonium Nickel Molybdate prepared by Chemical Precipitation, *Inorganic Chemistry*, Vol. 35, No. 14, p. 4191-4197 (1996). The preparation of such materials also has been reported by Teichner and Astier, *Appl. Catal.* 72, 321-29

(1991); Ann. Chim. Fr. 12, 337-43 (1987), and C. R. Acad. Sci. 304 (II), #11, 563-6 (1987) and Mazzocchia, Solid State Ionics, 63-65 (1993) 731-35.

Now, when molybdenum is partially substituted for by tungsten, an amorphous phase is produced which upon decomposition and, preferably, sulfidation, provides enhanced hydrodenitrogenation (HDN) catalyst activity relative to the unsubstituted (Ni-Mo) phase.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided a process for hydroprocessing a hydrocarbon feedstock, which process comprises contacting said feedstock, at hydroprocessing conditions, with a bulk catalyst comprised of at least one Group VIII metal and two Group VIB metals, which catalyst comprises a bulk metal catalyst containing non-noble Group VIII metal molybdate in which at least a portion but less than all of the molybdenum is replaced by tungsten. The hydroprocessing process is selected from at least one of hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, hydrodearomatization, hydroisomerization, hydrodewaxing, hydrotreating, hydrofining and hydrocracking.

In a specific embodiment of the present invention, there is provided a process for preparing a lubricating oil basestock containing at least about 90% saturates which comprises:

- (a) passing a feedstock to a hydrotreating zone containing at least one hydrotreating reactor containing a hydrotreating catalyst;

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(b) hydrotreating the feedstock in the presence of the hydrotreating catalyst under hydrotreating conditions wherein the hydrotreating catalyst is a bulk metal catalyst comprising non-noble Group VIII metal molybdate in which at least a portion but less than all of molybdenum is replaced by tungsten to produce a hydrotreated feedstock; and

(c) fractionating the hydrotreated feedstock.

In another embodiment of the invention, there is provided a process for preparing a lubricating oil basestock containing at least about 90% saturates which comprises:

(a) passing a feedstock to a first hydrotreating zone containing at least one hydrotreating reactor containing a first non-bulk metal hydrotreating catalyst;

(b) hydrotreating the feedstock in the presence of the first hydrotreating catalyst under first hydrotreating conditions wherein the first hydrotreating catalyst comprises at least one Group VIB and at least one non-noble Group VIII metal on a refractory oxide support to produce a first hydrotreated feedstock;

(c) passing at least a portion of the first hydrotreated feedstock to a second hydrotreating zone containing at least one hydrotreating reactor containing a second hydrotreating catalyst;

(d) hydrotreating the first hydrotreated feedstock in the second hydrotreating zone under second hydrotreating conditions wherein the second hydrotreating catalyst in said second hydrotreating zone is a bulk metal catalyst comprising non-noble Group VIII metal molybdate in which at least a portion

but less than all of molybdenum is replaced by tungsten to produce a second hydrotreated feedstock;

- (e) fractionating the second hydrotreated feedstock.

In yet another embodiment, there is provided a process for preparing a petroleum oil containing at least about 90% saturates which comprises:

- (a) passing a feedstock to a hydrotreating zone containing at least one hydrotreating reactor containing a hydrotreating catalyst;

- (b) hydrotreating the feedstock in the presence of the hydrotreating catalyst under hydrotreating conditions wherein the hydrotreating catalyst is a bulk metal catalyst comprising non-noble Group VIII metal molybdate in which at least a portion but less than all of molybdenum is replaced by tungsten to produce a hydrotreated feedstock;

- (c) fractionating the hydrotreated feedstock to produce a first basestock;

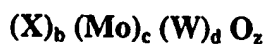
- (d) passing the first basestock to a hydrogenation zone containing at least one hydrogenation reactor containing a hydrogenation catalyst;

- (e) hydrogenating the first basestock in the presence of the hydrogenation catalyst under hydrogenation conditions wherein the hydrogenation catalyst comprises at least one Group VIII metal; and

- (f) fractionating the hydrogenated product from step (e) to produce a petroleum oil containing at least about 90% saturates.

In another preferred embodiment of the present invention the catalyst composition is prepared by a process which comprises contacting the Group VIII non-noble metal component with the Group VIB metal components in the presence of a protic liquid wherein during contacting not all of the Group VIB and/or Group VIII non-noble metals are in solution.

The preferred catalyst composition of the present invention can be further described as a bulk mixed metal oxide which is preferably sulfided prior to use, and which is represented by the formula:

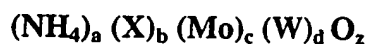


wherein X is non-noble Group VIII metal, the molar ratio of b: (c+d) is 0.5/1 to 3/1, preferably 0.75/1 to 1.5/1, more preferably 0.75/1 to 1.25/1;

The molar ratio of c:d is preferably >0.01/1, more preferably >0.1/1, still more preferably 1/10 to 10/1, still more preferably 1/3 to 3/1, most preferably substantially equimolar amounts of Mo and W, e.g., 2/3 to 3/2; and $z = [2b + 6(c+d)]/2$.

The essentially amorphous material has a unique X-ray diffraction pattern showing crystalline peaks at $d = 2.53$ Angstroms and $d = 1.70$ Angstroms.

The mixed metal oxide is readily produced by the decomposition of a precursor having the formula:



wherein the molar ratio of a:b is $\leq 1.0/1$, preferably 0-1; and X, b, c, and d, are as defined above, and $z = [a + 2b + 6(c+d)]/2$. The precursor has similar peaks at $d = 2.53$ and 1.70 Angstroms.

Decomposition of the precursor may be effected at elevated temperatures, e.g., temperatures of at least about 300°C , preferably about $300\text{-}450^{\circ}\text{C}$, in a suitable atmosphere, e.g., inerts such as nitrogen, argon, or steam, until decomposition is substantially complete, i.e., the ammonium is substantially completely driven off. Substantially complete decomposition can be readily established by thermogravimetric analysis (TGA), i.e., flattening of the weight change curve.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is the X-ray diffraction pattern of a $\text{NH}_4\text{Ni}_{1.5}\text{Mo}_{0.5}\text{W}_{0.5}$ compound prepared by boiling precipitation before calcining (Curve A) and after calcining at 400°C (Curve B). Note that the patterns for both the precursor and the decomposition product of the precursor are quite similar with the two peaks at essentially the same place. The ordinate is relative intensity; the abscissa is two theta (degrees).

Figure 2 shows the X-ray diffraction patterns, by $\text{CuK}\alpha$ radiation ($\lambda=1.5405\text{\AA}$), of $\text{NH}_4\text{-Ni-Mo}_{1-x}\text{-W}_x\text{-O}$ precursors wherein curve A is $\text{Mo}_{0.9}\text{W}_{0.1}$, curve B is $\text{Mo}_{0.7}\text{W}_{0.3}$, curve C is $\text{Mo}_{0.5}\text{W}_{0.5}$, curve D is $\text{Mo}_{0.3}\text{W}_{0.7}$, curve E is $\text{Mo}_{0.1}\text{W}_{0.9}$, and curve F is MoOW_1 . The ordinate and abscissa are as described for Figure 1.

PREFERRED EMBODIMENTS

The catalyst composition according to the invention can be used in virtually all hydroprocessing processes to treat a plurality of feeds under wide-ranging reaction conditions such as temperatures of from 200 to 450°C, hydrogen pressures of from 5 to 300 bar, liquid hourly space velocities of from 0.05 to 10 h⁻¹ and hydrogen treat gas rates of from 35.6 to 1780 m³/m³ (200 to 10000 SCF/B). The term "hydroprocessing" encompasses all processes in which a hydrocarbon feed is reacted with hydrogen at the temperatures and pressures noted above, and include hydrogenation, hydrotreating, hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, hydrodearomatization, hydroisomerization, hydrodewaxing, and hydrocracking including selective hydrocracking. Depending on the type of hydroprocessing and the reaction conditions, the products of hydroprocessing may show improved viscosities, viscosity indices, saturates content, low temperature properties, volatilities and depolarization. Feeds for hydroprocessing include reduced crudes, hydrocrackates, raffinates, hydrotreated oils, atmospheric and vacuum gas oils, coker gas oils, atmospheric and vacuum resids, deasphalted oils, dewaxed oils, slack waxes, Fischer-Tropsch waxes and mixtures thereof. It is to be understood that hydroprocessing of the present invention can be practiced in one or more reaction zones and can be practiced in either countercurrent flow or cocurrent flow mode. By countercurrent flow mode we mean a process mode wherein the feedstream flows countercurrent to the flow of hydrogen-containing treat gas.

The catalyst composition of the invention is particularly suitable for hydrotreating the hydrocarbon feeds suitable for hydroprocessing as noted above. Examples of hydrotreating include hydrogenation of unsaturates, hydrodesulfurization, hydrodenitrogenation, hydrodearomatization and mild hydrocracking. Conventional hydrotreating conditions include temperatures of from 250° to 450°C, hydrogen pressures of from 5 to 250 bar, liquid hourly space velocities of from 0.1 to 10 h⁻¹, and hydrogen treat gas rates of from 90 to 1780

m³/m³ (500 to 10000 SCF/B). The hydrotreating processes using the catalyst according to the invention may be particularly suitable for making lubricating oil basestocks meeting Group II or Group III base oil requirements.

A wide range of petroleum and chemical feedstocks can be hydroprocessed in accordance with the present invention. Suitable feedstocks range from the relatively light distillate fractions up to high boiling stocks such as whole crude petroleum, reduced crudes, vacuum tower residua, propane deasphalted residua, e.g., brightstock, cycle oils, FCC tower bottoms, gas oils including coker gas oils and vacuum gas oils, deasphalted residua and other heavy oils. The feedstock will normally be a C₁₀+ feedstock, since light oils will usually be free of significant quantities of waxy components. However, the process is also particularly useful with waxy distillate stocks, such as gas oils, kerosenes, jet fuels, lubricating oil stocks, heating oils, hydrotreated oil stock, furfural-extracted lubricating oil stock and other distillate fractions whose pour point and viscosity properties need to be maintained within certain specification limits. Lubricating oil stocks, for example, will generally boil above 230°C and more usually above 315°C. For purposes of this invention, lubricating oil or lube oil is that part of the hydrocarbon feedstock having a boiling point of at least 315°C, as determined by ASTM D-1160 test method.

The hydrocarbon feedstocks which are typically subjected to hydrotreating herein will typically boil at a temperature above 150 C. Examples of hydrocarbon feedstocks are those derived from at least one of thermal treatment, catalytic treatment, solvent extraction, dewaxing or fractionation of a petroleum crude or fraction thereof, shale oil, tar sand or synthetic crude. If desired, the feeds can be treated in a known or conventional manner to reduce sulfur and/or nitrogen content thereof. Preferred feeds are waxy or dewaxed vacuum gas oil distillates, waxy or dewaxed hydrotreated or hydrocracked

vacuum gas oil distillates and waxy or dewaxed solvent extracted raffinates boiling above 315 C.

The process of the invention is used to prepare highly saturated basestocks or other petroleum oils. These basestocks can be used to meet the requirements of Group II or Group III basestocks. The petroleum oils meet the requirements of technical or medicinal grade white oils which requirements include high saturates content and low color and toxicity. The bulk metal catalyst according to the invention may be used either alone or in combination with hydrotreating or hydrogenation catalysts. When used alone, the process for preparing a lubricating oil basestock comprises hydrotreating a feedstock in the presence of the bulk metal catalyst. The hydrotreating conditions include temperatures of from 250 to 400 °C, hydrogen pressures of from 500 to 3500 psig (3549 to 24234 kPa), liquid hourly space velocities of from 0.1 to 5.0 and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³).

The first hydrotreating zone may be followed with a hydrogenation zone. The catalyst in the hydrogenation zone may be a conventional non-bulk metal hydrotreating catalyst as described below or may contain at least one Group VIII noble metal such as platinum and/or palladium. Also included as hydrogenation catalyst are conventional bulk or non-bulk metal catalysts such as those containing nickel. The hydrogenation catalyst may be promoted with a promoter such as a halogen, e.g., chlorine or fluorine. The hydrogenation conditions include temperatures of from 150 to 400 °C, hydrogen pressures of from 500 to 3500psig (3549 to 24234 kPa), liquid hourly space velocities of from 0.1 to 5.0 and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³).

The subject catalyst may also be combined in hydrotreating processes using conventional non-bulk metal hydrotreating catalyst. In one embodiment,

feedstock is first hydrotreated in a hydrotreating zone containing a non-bulk metal hydrotreating catalyst. Preferred non-bulk metal catalysts include at least one Group VIB metal such as molybdenum or tungsten and at least one non-noble metal Group VIII such as cobalt or nickel. Hydrotreating conditions include temperatures of from 250 to 400 °C, hydrogen pressures of from 500 to 3500 psig (3549 to 24234 kPa), liquid hourly space velocities of from 0.1 to 5.0 and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³). The product from the first hydrotreating zone is then hydrotreated in a second hydrotreating zone containing bulk metal catalyst according to the invention under the same hydrotreating conditions as present in the first hydrotreating zone.

The process according to the invention may be used to prepare lubricating basestocks and other petroleum oils containing saturates of at least about 90%, preferably greater than about 95%, especially greater than about 98%. Such lubricating oil basestocks meet the requirements of Group II or Group III passenger car motor oils. Highly saturated petroleum oils can be used to meet the requirements of technical and medicinal white oils. Medicinal white oils typically have greater than 99% saturates.

White mineral oils, called white oils, are colorless, transparent, oily liquids obtained by the refining of crude petroleum feedstocks. In the production of white oils, an appropriate petroleum feedstock is refined to eliminate, as completely as possible, oxygen, nitrogen, and sulfur compounds, reactive hydrocarbons including aromatics, and any other impurity which would prevent use of the resulting white oil in the pharmaceutical or food industry.

The hydrocarbon feedstocks which are typically subjected to hydrocracking herein will typically boil at a temperature above 150°C. The feedstocks can contain a substantial amount of nitrogen, e.g. at least 10 wppm

nitrogen, and even greater than 500 wppm, in the form of organic nitrogen compounds. The feeds can also have a significant sulfur content, ranging from about 0.1 wt.% to 3 wt.%, or higher. If desired, the feeds can be treated in a known or conventional manner to reduce the sulfur and/or nitrogen content thereof.

For purposes of the present invention where it is desirable to produce a lube basestock the feed can be a wide variety of wax-containing feedstocks including feeds derived from crude oils, shale oils and tar sands as well as synthetic feeds such as those derived from the Fischer-Tropsch process. Typical wax-containing feedstocks for the preparation of lubricating base oils have initial boiling points of about 315° C or higher, and include feeds such as reduced crudes, hydrocrackates, raffinates, hydrotreated oils, atmospheric gas oils, vacuum gas oils, coker gas oils, atmospheric and vacuum resids, deasphalted oils, slack waxes and Fischer-Tropsch wax. The feed is preferably a mixture of gas oil from a coker and vacuum distillation from conventional crudes with a maximum boiling point of the coker gas oil not to exceed 1050°F. Such feeds may be derived from distillation towers (atmospheric and vacuum), hydrocrackers, hydrotreaters and solvent extraction units, and may have wax contents of up to 50% or more.

The feedstream is contacted at hydroprocessing conditions with a bulk catalyst containing two Group VIB metal and at least one Group VIII metal, preferably two Group VIB-metals and one non-noble Group VIII metal, more preferably Ni-Mo-W. The bulk catalyst compositions of the present invention can be prepared by a process wherein all of the metal precursor components are in solution or where not all of the metal components are in solution. That is, a process which comprises contacting at least one Group VIII non-noble metal component with the Group VIB metal components in the presence of a protic

liquid wherein during contacting not all of the Group VIB and/or Group VIII non-noble metals are in solution.

Process for preparing catalyst wherein not all of the metals are in solution.

Generally, the contacting of the metal components in the presence of the protic liquid comprises mixing the metal components and subsequently reacting the resulting mixture. It is essential to the solid route that at least one metal components is added at least partly in the solid state during the mixing step and that the metal of at least one of the metal components which have been added at least partly in the solid state, remains at least partly in the solid state during the mixing and reaction step. "Metal" in this context does not mean the metal in its metallic form but present in a metal compound, such as the metal component as initially applied or as present in the bulk catalyst composition.

Generally, during the mixing step either at least one metal component is added at least partly in the solid state and at least one metal component is added in the solute state, or all metal components are added at least partly in the solid state, wherein at least one of the metals of the metal components which are added at least partly in the solid state remains at least partly in the solid state during the entire process of the solid route. That a metal component is added "in the solute state" means that the whole amount of this metal component is added as a solution of this metal component in the protic liquid. That a metal component is added "at least partly in the solid state" means that at least part of the metal component is added as solid metal component and, optionally, another part of the metal component is added as a solution of this metal component in the protic liquid. A typical example is a suspension of a metal component in a protic liquid in which the metal is at least partly present as a solid, and optionally partly dissolved in the protic liquid.

If during the mixing step at least one metal component is added at least partly in the solid state and at least one metal component is added in the solute state, the following process alternatives can be applied: it is possible to first prepare a suspension of a metal component in the protic liquid and to add simultaneously, or one after the other, solutions and/or further suspensions comprising dissolved and/or suspended metal components in the protic liquid. It is also possible to first combine solutions either simultaneously or one after the other and to subsequently add further suspensions and optionally solutions either simultaneously or one after the other. If during the mixing step, each metal component is added at least partly in the solid state, it is possible to prepare suspensions comprising the metal components and to combine these suspensions either one after the other or simultaneously. It is also possible to add the metal components as such to a suspension or solution of at least one of the metal components.

In all the above-described cases, the suspension comprising a metal component can be prepared by suspending a preformed metal component in the protic liquid. However, it is also possible to prepare the suspension by (co) precipitating one or more metal components in the protic liquid. The resulting suspension can either be applied as such in the process of the solid route, i.e. further metal components either in solution, slurry or *per se* are added to the resulting suspension, or it can be applied after solid-liquid separation and optionally re-slurrying of the obtained solid metal component in the protic liquid.

Further, in all the above cases, instead of a suspension of a metal component, it is also possible to use a metal component in the wetted or dry state. Wetted or dry metal components can be prepared from preformed metal components or by precipitation as described above and by subsequently partly or

completely removing the protic liquid. However, care must be taken that any protic liquid is present during contacting.

It must be noted that the above process alternatives are only some examples to illustrate the mixing step. Independently from the number of metal components that are applied in the solid route, the order of addition is generally not critical to the process of this invention.

In one embodiment of the present invention (solid route), one of the metal components is added at least partly in the solid state and further metal components are added in the solute state. For instance, one metal component is added at least partly in the solid state and two metal components are added in the solute state. In another embodiment, two metal components are added at least partly in the solid state and one metal component is added in the solute state. In still another embodiment, three or more metal components are added at least partly in the solid state and no further metal components are added in the solute state. Generally, the number of metal components which are added at least partly in the solid state and which are added in the solute state is not critical to the this invention.

It will be clear that it is, e.g., not suitable to prepare first a solution comprising all metal components necessary for the preparation of a certain catalyst composition and to subsequently coprecipitate these components. Nor is it suitable for the process for the this invention to add metal components at least partly in the solid state and to choose the process conditions, such as temperature, pH or amount of protic liquid in such a way, that all added metal components are present at least at some stage completely in the solute state. On the contrary, as has been set out above, for the solid route, at least the metal of

one of the metal components that are added at least partly in the solid state must remain in at least partly the solid state during the entire process of this invention.

Preferably, at least 1 wt.%, even more preferably at least 10 wt.% and most preferably at least 15 wt.% of the metal components are in the solid state during mixing, based on the total weight of all added metal components, i.e., of all metal components employed initially in the solid route, calculated as metal oxides. When it is desired to obtain a high yield, i.e., a high amount of the bulk catalyst composition, the use of metal components of which a high amount remains in the solid state during contacting is recommended. As in this case, low amounts of metal components remain solved in the mother liquid, the amount of metal components ending up in the wastewater during the subsequent solid-liquid separation is decreased.

If the metals which are added at least partly in the solid state are added as a suspension, the amount of solid metals in this suspension can be determined by filtration of the suspension at the conditions which are applied during the mixing step (temperature, pH, pressure, amount of liquid) in such a way that all solid material contained in the suspension is collected as solid filter cake. From the weight of the solid and dried filter cake, the weight of the solid metals can be determined by standard techniques. If several suspensions are applied, the weight of the solid metal components contained in these suspensions must be added to each other to give the total amount of solid metal components, calculated as metal oxides. Of course, if apart from solid metal components further solid components such as a solid binder are present in the filter cake, the weight of this solid and dried binder must be subtracted from the weight of the metal components in the solid and dried filter cake. In this case, standard techniques such as atomic absorption spectroscopy (AAS), XRF, wet chemical analysis, or ICP can determine the amount of solid metals in the filter cake.

If the metal component, which is added at least partly in the solid state, is added in the wetted or dry state, a filtration generally is not possible. In this case, the weight of the solid metal component is considered equal to the weight of the corresponding initially employed metal component. The total weight of all metal components is the amount of all metals that are initially employed as metal components, calculated as metal oxides.

It has been found that the morphology and texture of the metal component, which remains at least partly in the solid state during contacting, may determine the morphology and texture of the bulk catalyst composition. Consequently, e.g., by applying metal component particles with a certain morphology and texture, the morphology and texture of the resulting bulk catalyst particles can be controlled. "Morphology and texture" in the sense of the present invention refer to pore volume, pore size distribution, surface area, particle form, and particle size.

To obtain a bulk catalyst composition with high catalytic activity, it is therefore preferred that the metal components, which are at least partly in the solid state during contacting, are porous metal components. It is desired that the total pore volume and pore size distribution of these metal components is approximately the same as those of conventional hydrotreating catalysts. Conventional hydrotreating catalysts generally have a pore volume of 0.05 - 5 ml/g, preferably of 0.1 - 4 ml/g, more preferably of 0.1 - 3 ml/g and most preferably of 0.1 - 2 ml/g determined by nitrogen adsorption. Pores with a diameter smaller than 1 nm are generally not present in conventional hydrotreating catalysts. Further, conventional hydrotreating catalysts have generally a surface area of at least 10 m²/g and more preferably of at least 50 m²/g and most preferably of at least 100 m²/g, determined VIB the B.E.T.

method. For instance, nickel carbonate can be chosen which has a total pore volume of 0.19 - 0.39 ml/g and preferably of 0.24 - 0.35 ml/g determined by nitrogen adsorption and a surface area of 150 - 400 m²/g and more preferably of 200 - 370 m²/g determined by the B.E.T. method. Furthermore these metal components should have a median particle diameter of at least 50 nm, more preferably at least 100 nm, and preferably not more than 5000 µm and more preferably not more than 3000 µm. Even more preferably, the median particle diameter lies in the range of 0.1 - 50 µm and most preferably in the range of 0.5 - 50 µm. For instance, by choosing a metal component which is added at least partly in the solid state and which has a large median particle diameter, the other metal components will only react with the outer layer of the large metal component particle. In this case, so-called "core-shell" structured bulk catalyst particles are obtained.

An appropriate morphology and texture of the metal component can either be achieved by applying suitable preformed metal components or by preparing these metal components by the above-described precipitation under such conditions that a suitable morphology and texture is obtained. A proper selection of appropriate precipitation conditions can be made by routine experimentation.

As has been set out above, to retain the morphology and texture of the metal components which are added at least partly in the solid state, it is essential that the metal of the metal component at least partly remains in the solid state during the whole process of this solid route. It is noted again that it is essential that in no case should the amount of solid metals during the process of the solid route becomes zero. The presence of solid metal comprising particles can easily be detected by visual inspection at least if the diameter of the solid particles in which the metals are comprised is larger than the wavelength of visible light. Of

course, methods such as quasi-elastic light scattering (QELS) or near forward scattering which are known to the skilled person can also be used to ensure that in no point in time of the process of the solid route, all metals are in the solute state.

Without wishing to be bound by any theory, it is believed that during the process of the solid route, the metal components, which are added during the mixing step at least partly, react with each other. The protic liquid is responsible for the transport of dissolved metal components. Due to this transport, the metal components come into contact with each other and can react. It is believed that this reaction can even take place if all metal components are virtually completely in the solid state. Due to the presence of the protic liquid, a small fraction of metal components may still dissolve and consequently react as described above. The presence of a protic liquid during the process of the solid route is therefore considered essential. The reaction can be monitored by any conventional technique such as IR spectroscopy, Raman spectroscopy, or by monitoring the pH of the reaction mixture.

In one preferred embodiment of the solid route, during mixing not all metal components are added completely in the solid state. Preferably, at least 0.1 wt.%, more preferably at least 0.5 wt.% and still more preferably at least 1 wt.% of the metal components initially employed in the solid route are added as a solution during the mixing step, calculated as metal oxides. In this way, proper contacting of the metal components is ensured.

The protic liquid to be applied in the solid or solution route of this invention for preparing catalyst can be any protic liquid. Examples include water, carboxylic acids, and alcohols such as methanol or ethanol. Preferably, a liquid comprising water such as mixtures of an alcohol and water and more

preferably water is used as protic liquid in this solid route. Also different protic liquids can be applied simultaneously in the solid route. For instance, it is possible to add a suspension of a metal component in ethanol to an aqueous solution of another metal component. In some cases, a metal component can be used which dissolves in its own crystal water. The crystal water serves as protic liquid in this case.

The molar ratio of Group VIB to Group VIII non-noble metals applied in the solid route ranges generally from 10:1 - 1:10 and preferably from 3:1 - 1:3. In the case of core-shell structured particles, these ratios may lie outside the above ranges. If more than one Group VIB metal is used, the ratio of the different Group VIB metals is generally not critical. The same holds when more than one Group VIII non-noble metal is used. In the case where molybdenum and tungsten are applied as Group VIB metals, the molybdenum:tungsten ratio preferably lies in the range of 9:1 - 1:9.

The Group VIB metal generally comprises chromium, molybdenum, tungsten, or mixtures thereof. Suitable Group VIII non-noble metals are, e.g., iron, cobalt, nickel, or mixtures thereof. Preferably, a combination of metal components comprising nickel, molybdenum and tungsten or nickel, cobalt, molybdenum and tungsten is applied in the process of the solid route. If the protic liquid is water, suitable nickel components which are at least partly in the solid state during contacting comprise water-insoluble nickel components such as nickel carbonate, nickel hydroxide, nickel phosphate, nickel phosphite, nickel formate, nickel sulfide, nickel molybdate, nickel tungstate, nickel oxide, nickel alloys such as nickel-molybdenum alloys, Raney nickel, or mixtures thereof. Suitable molybdenum components, which are at least partly in the solid state during contacting, comprise water-insoluble molybdenum components such as molybdenum (di- and tri) oxide, molybdenum carbide, molybdenum nitride,

aluminum molybdate, molybdic acid (e.g., H_2MoO_4), molybdenum sulfide, or mixtures thereof. Finally, suitable tungsten components which are at least partly in the solid state during contacting comprise tungsten di- and trioxide, tungsten sulfide (WS_2 and WS_3), tungsten carbide, tungstic acid (e.g., $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$, $\text{H}_2\text{W}_4\text{O}_{13} \cdot 9\text{H}_2\text{O}$), tungsten nitride, aluminum tungstate (also meta-, or polytungstate) or mixtures thereof. These components are generally commercially available or can be prepared by, e.g., precipitation. e.g., nickel carbonate can be prepared from a nickel chloride, sulfate, or nitrate solution by adding an appropriate amount of sodium carbonate. It is generally known to the skilled person to choose the precipitation conditions in such a way as to obtain the desired morphology and texture.

In general, metal components, which mainly contain C, O. and/or H beside the metal, are preferred because they are less detrimental to the environment. Nickel carbonate is a preferred metal component to be added at least partly in the solid state because when nickel carbonate is applied, CO_2 evolves and positively influences the pH of the reaction mixture. Further, due to the transformation of carbonate into CO_2 , the carbonate does not end up in the wastewater.

Preferred nickel components which are added in the solute state are water-soluble nickel components, e.g. nickel nitrate, nickel sulfate, nickel acetate, nickel chloride, or mixtures thereof. Preferred molybdenum and tungsten components which are added in the solute state are water-soluble molybdenum and tungsten components such as alkali metal or ammonium molybdate (also peroxy-, di-, tri-, tetra-, hepta-, octa-, or tetradecamolybdate), Mo-P heteropolyanion compounds, W-Si heteropolyanion compounds, W-P heteropolyanion compounds, W-Si heteropolyanion compounds, Ni-Mo-W heteropolyanion compounds, Co-Mo-W heteropolyanion compounds, alkali

metal or ammonium tungstates (also meta-, para-, hexa-, or polytungstate), or mixtures thereof.

Preferred combinations of metal components are nickel carbonate, tungstic acid and molybdenum oxide. Another preferred combination is nickel carbonate, ammonium dimolybdate and ammonium metatungstate. It is within the scope of the skilled person to select further suitable combinations of metal components. It must be noted that nickel carbonate always comprises a certain amount of hydroxy-groups. It is preferred that the amount of hydroxy-groups present in the nickel carbonate be high.

In the following, preferred process conditions during the mixing and subsequent reaction step shall be described:

a) Mixing step:

The process conditions during the mixing step are generally not critical. It is, e.g., possible to add all components at ambient temperature at their natural pH (if a suspension or solution is applied). Generally, it is of course preferred to keep the temperature below the boiling point of the protic liquid, i.e., 100°C in the case of water to ensure easy handling of the components during the mixing step. However, if desired also temperatures above the boiling point of the protic liquid or different pH values can be applied. If the reaction step is carried out at increased temperatures, the suspensions and solutions which are added during the mixing step are generally preheated to an increased temperature which can be equal to the reaction temperature.

b) Reaction step:

After all metal components have been mixed, they are generally agitated at a certain temperature for a certain period of time to allow the reaction to take place. The reactio

point of the protic liquid, such as 100°C in the case of water, the process is generally carried out at atmospheric pressure. Above this temperature, the reaction is general more preferably in the range of 3 - 8. As has been set out above, care must be taken that the

The reaction time generally lies in the range of 1 minute to several days, more preferably 1 minute to 24 hours, and most preferably in the range of 5 minutes to 10 hours. As has been mentioned above, the reaction time depends on the temperature.

Process step (i) according to the solution route

As mentioned above, alternatively to the above-described solid route for step (i), it is also possible to prepare the bulk catalyst composition by a process comprising reacting in a reaction mixture a Group VIII non-noble metal component in solution and a Group VIB metal component in solution to obtain a precipitate. As in the case of the solid route, preferably, one Group VIII non-noble metal component is reacted with two Group VIB metal components. The molar ratio of Group VIB metals to Group VIII non-noble metals applied in the process of the solution route is preferably the same as described for the solid route. Suitable Group VIB and Group VIII non-noble metal components are, e.g. those water-soluble nickel, molybdenum and tungsten components described above for the solid route. Further Group VIII non-noble metal components are, e.g., cobalt or iron components. Further Group VIB metal components are, e.g. chromium components. The metal components can be added to the reaction mixture in solution, suspension or as such. If soluble salts are added as such, they will dissolve in the reaction mixture and subsequently be precipitated.

The reaction mixture is reacted to obtain a precipitate. Precipitation is effected by adding a Group VIII non-noble metal salt solution at a temperature and pH at

which the Group VIII non-noble metal and the Group VIB metal precipitate, adding a compound which complexes the metals and releases the metals for precipitation upon temperature increase or pH change or adding a Group VIB metal salt solution at a temperature and pH at which the Group VIII non-noble metal and Group VIB metal precipitate, changing the temperature, changing the pH, or lowering the amount of the solvent. The precipitate obtained with this process appears to have high catalytic activity. In contrast to the conventional hydroprocessing catalysts, which usually comprise a carrier impregnated with Group VIII non-noble metals and Group VIB metals, said precipitate can be used without a support. Unsupported catalyst compositions are usually referred to as bulk catalysts. Changing the pH can be done by adding base or acid to the reaction mixture, or adding compounds, which decompose upon temperature increase into hydroxide ions or H^+ ions that respectively increase or decrease the pH. Examples of compounds that decompose upon temperature increase and thereby increase or decrease the pH are urea, nitrites, ammonium cyanate, ammonium hydroxide, and ammonium carbonate.

In an illustrative process according to the solution route, solutions of ammonium salts of a Group VIB metal are made and a solution of a Group VIII non-noble metal nitrate is made. Both solutions are heated to a temperature of approximately 90°C. Ammonium hydroxide is added to the Group VIB metal solution. The Group VIII non-noble metal solution is added to the Group VIB metal solution and direct precipitation of the Group VIB and Group VIII non-noble metal components occurs. This process can also be conducted at lower temperature and/or decreased pressure or higher temperature and/or increased pressure.

In another illustrative process according to the solution route, a Group VIB metal salt, a Group VIII metal salt, and ammonium hydroxide are mixed in solution

together and heated so that ammonia is driven off and the pH is lowered to a pH at which precipitation occurs. For instance when nickel, molybdenum, and tungsten components are applied, precipitation typically occurs at a pH below 7.

Independently from whether the solid or solution route is chosen in step (i), the resulting bulk catalyst composition preferably comprises and more preferably consists essentially of bulk catalyst particles having the characteristics of the bulk catalyst particles described under the heading "Catalyst compositions of the invention."

The bulk catalyst composition of step (i) can generally be directly shaped into hydroprocessing particles. If the amount of liquid of the bulk catalyst composition resulting from step (i) is so *high* that it cannot be directly subjected to a shaping step, a solid liquid separation can be performed before shaping. Optionally the bulk catalyst composition, either as such or after solid liquid separation, can be calcined before shaping.

Process step (ii)

It is preferred to add a binder material during the process of the invention. More in particular, a binder material can be added during the preparation of the bulk catalyst composition and/or the bulk catalyst composition can be composited with a binder material before the shaping step. The latter alternative is generally preferred. The binder material can be added in the dry state, either calcined or not, in the wetted and/or suspended state and/or as solution. As has been mentioned above, "binder material" in the sense of the present invention refers to a binder and/or a precursor thereof.

If the binder material is added during the preparation of the bulk catalyst composition, the following options are available: If, e g., the bulk catalyst composition in step (i) is prepared according to the solid route, the metal components can be added to the binder material either simultaneously or one after the other. Alternatively, the metal components can be combined as described above and subsequently a binder material can be added to the combined metal components. It is further possible to combine part of the metal components either simultaneously or one after the other, to subsequently add the binder material and to finally add the rest of the metal components either simultaneously or one after the other. For instance, the metal component which is at least partly in the solid state during contacting can be first mixed and if desired shaped with the binder material and subsequently, further metal components can be added to the optionally shaped mixture. However, it is also possible to combine the binder with metal components in the solute state and to subsequently add a metal component at least partly in the solid state. Finally, simultaneous addition of the metal components and the binder material is possible. Moreover, the binder material can be added during the reaction step of the solid route in step (i).

If the solution route is applied in step (i), the binder material can be added to the reaction mixture either in combination or not with one or more of the metal components before or after precipitation.

If the binder material is added as a solution, care must be taken that the binder will be converted into the solid state during the process of the invention. This can be done by adjusting the pH conditions during step (i) in such a way that precipitation of the binder occurs. Suitable conditions for the precipitation of the binder are known to the skilled person and need no further explanation. If the amount of liquid of the resulting bulk catalyst - binder composition is too high,

optionally a solid liquid separation can be carried out. Following the preparation of the bulk catalyst- binder composition and optional solid liquid separation, the bulk catalyst - binder composition can be shaped directly. Optionally, the bulk catalyst - binder composition can be calcined and subsequently re-wetted prior to shaping. This is especially preferred in the case where the bulk catalyst composition has been prepared via the solution route using nitrate and/or ammonium salts. Moreover, additional binder material can be added subsequent to the preparation of the above bulk catalyst binder composition.

As has been set out above, it is preferred to first prepare the bulk catalyst composition and to subsequently composite the resulting bulk catalyst composition with the binder material. Optionally, the bulk catalyst composition can be subjected to a solid-liquid separation before being composited with the binder material. After solid-liquid separation, optionally, a washing step can be included. Further, it is possible to calcine the bulk catalyst composition after an optional solid liquid separation and drying step and prior to compositing it with the binder material.

In all the above-described process alternatives, the term "compositing the bulk catalyst composition with a binder material" means that the binder material is added to the bulk catalyst composition or vice versa and the resulting composition is mixed.

As has been set out above, the median diameter of the bulk catalyst particles is at least 50 nm, more preferably at least 100 nm, and preferably not more than 5000 μm and more preferably not more than 3000 μm . Even more preferably, the median particle diameter lies in the range of 0.1 - 50 μm and most preferably in the range of 0.5-50 μm .

Binder materials to be applied in the process of the invention may be any materials that are conventionally applied as a binder in hydroprocessing catalysts. Examples include silica, silica-alumina, such as conventional silica-alumina, silica-coated alumina and alumina-coated silica, alumina such as (pseudo) boehmite, or gibbsite, titania, zirconia, cationic clays or anionic clays such as saponite, bentonite, kaoline, sepiolite or hydrotalcite, or mixtures thereof. Preferred binders are silica, silica-alumina, alumina, titanic, zirconia, or mixtures thereof. These binders may be applied as such or after peptization. It is also possible to apply precursors of these binders that, during the process of the invention are converted into any of the above-described binders. Suitable precursors are, e.g., alkali metal aluminates (to obtain an alumina binder), water glass (to obtain a silica binder), a mixture of alkali metal aluminates and water glass (to obtain a silica alumina binder), a mixture of sources of a di-, tri-, and/or tetravalent metal such as a mixture of water-soluble salts of magnesium, aluminum and/or silicon (to prepare a cationic clay and/or anionic clay), chlorohydrol, aluminum sulfate, or mixtures thereof.

If desired, the binder material may be composited with a Group VIB metal and/or a Group VIII non-noble metal, prior to being composited with the bulk catalyst composition and/or prior to being added during the preparation thereof. Compositing the binder material with any of these metals may be carried out by impregnation of the solid binder with these materials. The person skilled in the art knows suitable impregnation techniques. If the binder is peptized, it is also possible to carry out the peptization in the presence of Group VIB and/or Group VIII non-noble metal components.

If alumina is applied as binder, the surface area preferably lies in the range of 100 - 400 m²/g, and more preferably 150 - 350 m²/g, measured by the B.E.T.

method. The pore volume of the alumina is preferably in the range of 0.5 - 1.5 ml/g measured by nitrogen adsorption.

Generally, the binder material to be added in the process of the invention has less catalytic activity than the bulk catalyst composition or no catalytic activity at all. Consequently, by adding a binder material, the activity of the bulk catalyst composition may be reduced. Therefore, the amount of binder material to be added in the process of the invention generally depends on the desired activity of the final catalyst composition. Binder amounts from 0 - 95 wt.% of the total composition can be suitable, depending on the envisaged catalytic application. However, to take advantage of the resulting unusual high activity of the composition of the present invention, binder amounts to be added are generally in the range of 0.5 - 75 wt.% of the total composition.

If in the process of the invention, a binder material is used, the resulting catalyst composition comprises the bulk catalyst particles obtained in step (i) imbedded in the binder material. In other words, during the process of the invention, the bulk catalyst particles generally do not disintegrate but normally, the morphology of the bulk catalyst particles is essentially maintained in the resulting catalyst composition.

Process step (iii)

The catalyst composition resulting from the above-described process alternatives can be directly shaped. Shaping comprises extrusion, pelletizing, beading, and/or spray drying. It must be noted that if the catalyst composition is to be applied in slurry type reactors, fluidized beds, moving beds, expanded beds, or ebullating beds, spray drying or beading is generally applied for fixed bed applications, generally, the catalyst composition is extruded, pelletized and/or

beaded. In the latter case, prior to or during the shaping step, any additives that are conventionally used to facilitate shaping can be added. These additives may comprise aluminum stearate, surfactants, graphite or mixtures thereof. These additives can be added at any stage prior to the shaping step. Further, when alumina is used as a binder, it may be desirable to add acids prior to the shaping step such as nitric acid to increase the mechanical strength of the extrudates.

It is preferred that a binder material is added prior to the shaping step. Further, it is preferred that the shaping step is carried out in the presence of a liquid, such as water. Preferably, the amount of liquid in the extrusion mixture, expressed as LOI is in the range of 20 - 80%

The resulting shaped catalyst composition can, after an optional drying step, be optionally calcined. Calcination however is not essential to the process of the invention. If a calcination is carried out in the process of the invention, it can be done at a temperature of, e.g., from 100° - 600°C and preferably 350° to 500°C for a time varying from 0.5 to 48 hours. The drying of the shaped particles is generally carried out at temperatures above 100°C.

Additional process steps:

In a preferred embodiment of the invention, the catalyst composition is subjected to spray drying, (flash) drying, milling, kneading, or combinations thereof prior to shaping. These additional process steps can be conducted either before or after a binder is added, after solid-liquid separation, before or after calcination and subsequent to re-wetting. It is believed that by applying any of the above-described techniques of spray drying, (flash) drying, milling, kneading, or combinations thereof, the degree of mixing between the bulk catalyst composition and the binder material is improved. This applies to both cases

where the binder material is added before or after the application of any of the above-described methods. However, it is generally preferred to add the binder material prior to spray drying and/or any alternative technique. If the binder is added subsequent to spray drying and/or any alternative technique, the resulting composition is preferably thoroughly mixed by any conventional technique prior to shaping. An advantage of, e.g., spray drying is that no wastewater streams are obtained when this technique is applied.

It must be noted that combinations of the above-described processes with respect to the binder addition can be applied. For instance, part of the binder material can be added during the preparation of the bulk catalyst composition and part of the binder material can be added at any subsequent stage prior to shaping. Further, it is also possible to apply more than one of the above-described techniques.

In all the above process steps the amount of liquid must be controlled. If, e.g., prior to subjecting the catalyst composition to spray drying, the amount of liquid is too low, additional liquid must be added. If, on the other hand, e.g. prior to extrusion of the catalyst composition, the amount of liquid is too high, the amount of liquid must be reduced by, e.g., solid liquid separation via, e.g., filtration, decantation, or evaporation and, if necessary, the resulting material can be dried and subsequently be re-wetted to a certain amount. For all the above process steps, it is within the scope of the skilled person to control the amount of liquid appropriately. Generally, it may be preferred to choose the amount of liquid during the process steps (i) and (ii) in such a way that no additional drying step is necessary prior to applying spray drying and/or any alternative technique or shaping. Further, it is preferred to carry out any of the above techniques in such a way that the resulting, e.g., spray dried and/or kneaded composition contains an amount of liquid which allows the composition to be directly shaped.

Spray drying is preferably carried out at an outlet temperature in the range of 100° - 200°C and more preferably 120° - 180°C.

Apart from the binder materials described above, it is also possible to add conventional hydrodenitrogenation catalysts. These catalysts can be added in the spent, regenerated, or fresh state. In principle, it is hydroprocessing catalysts such as conventional hydrodesulfurization and possible to add these catalysts instead of a binder material or precursor thereof. In other words, it is possible to carry out all the above-described process alternatives wherein the binder material or precursor thereof is replaced fully or in part by a conventional hydroprocessing catalyst. In principle, the conventional hydroprocessing catalyst can be added at any stage of the process of the present invention prior to the shaping step. Within the context of this description, "at any stage of the process prior to the shaping step" means: it can be added during the preparation of the bulk catalyst composition, and/or subsequent to the preparation of the bulk catalyst composition but prior to the addition of the binder material, and/or during, and/or subsequent to the addition of the binder material, but prior to spray drying or any alternative method, and/or during and/or subsequent to spray drying or any alternative method but prior to the shaping step it is possible to add a conventional hydroprocessing catalyst during the compositing step (ii) with the binder. If desired, the conventional hydroprocessing catalyst may be milled before being applied in the process of the invention.

Furthermore, a cracking component may be added during the process of the present invention. A cracking component in the sense of the present invention is any conventional cracking component such as cationic clays, anionic clays, zeolites such as ZSM-5, (ultra-stable) zeolite Y, zeolite X, ALPO's, SAPO's, amorphous cracking components such as silica-alumina, or mixtures thereof. It will be clear that some materials may act as a binder and a cracking component

at the same time. For instance, silica-alumina may have at the same time a cracking and a binding function.

If desired, the cracking component may be composited with a Group VIB metal and/or a Group VIII non-noble metal prior to being composited with the bulk catalyst composition and/or prior to being added during the preparation thereof. Compositing the cracking component with any of these metals may be carried out by impregnation of the cracking component with these materials.

The cracking component can be added at any stage of the process of the present invention prior to the shaping step. However, it is preferred to add the cracking component during the compositing step (ii) with the binder.

Generally, it depends on the envisaged catalytic application of the final catalyst composition which of the above-described cracking components is added. A zeolite is preferably added if the resulting composition shall be applied in hydrocracking or fluid catalytic cracking. Other cracking components such as silica-alumina or cationic clays are preferably added if the final catalyst composition shall be used in hydrotreating applications. The amount of cracking material that is added depends on the desired activity of the final composition and the application envisaged and thus may vary from 0 - 80 wt.%, based on the total weight of the catalyst composition.

If desired, further materials can be added in addition to the metal components already added in step (i). These materials include any material that is added during conventional hydroprocessing catalyst preparation. Suitable examples are phosphorus compounds, borium compounds, fluor-containing compounds, additional transition metals, rare earth metals, fillers, or mixtures thereof.

Suitable phosphorus compounds include ammonium phosphate, phosphoric acid, or organic phosphorus compounds. Phosphorus compounds can be added at any stage of the process of the present invention prior to the shaping step and/or subsequent to the shaping step. If the binder material is peptized, phosphorus compounds can also be used for peptization. For instance, the binder can be peptized by contacting the binder with phosphoric acid or with a mixture of phosphoric and nitric acid.

Suitable additional transition metals are, e.g., rhenium, ruthenium, rhodium, iridium, chromium, vanadium, iron, cobalt, platinum, palladium, cobalt, nickel, molybdenum, or tungsten. Nickel, molybdenum, and tungsten can be applied in the form of any of the water-insoluble nickel, molybdenum and/or tungsten components that are described above for the solid route. These metals can be added at any stage of the process of the present invention prior to the shaping step. Apart from adding these metals during the process of the invention, it is also possible to composite the final catalyst composition therewith. It is, e.g., possible to impregnate the final catalyst composition with an impregnation solution comprising any of these metals.

The processes of the present invention for preparing the bulk catalyst compositions may further comprise a sulfidation step. Sulfidation is generally carried out by contacting the catalyst composition or precursors thereof with a sulfur containing compound such as elementary sulfur, hydrogen sulfide or polysulfides. The sulfidation can generally be carried out subsequently to the preparation of the bulk catalyst composition but prior to the addition of a binder material, and/or subsequently to the addition of the binder material but prior to subjecting the catalyst composition to spray drying and/or any alternative method, and/or subsequently to subjecting the composition to spray drying and/or any alternative method but prior to shaping, and/or subsequently to shaping the

catalyst composition. It is preferred that the sulfidation is not carried out prior to any process step that reverts the obtained metal sulfides into their oxides. Such process steps are, e.g., calcination or spray drying or any other high temperature treatment in the presence of oxygen. Consequently, if the catalyst composition is subjected to spray drying and/or any alternative technique, the sulfidation should be carried out subsequent to the application of any of these methods.

Additionally to, or instead of, a sulfidation step, the bulk catalyst composition may be prepared from at least one metal sulfide. If, e.g., the solid route is applied in step (i), the bulk catalyst component can be prepared from nickel sulfide and/or molybdenum sulfide and/or tungsten sulfide.

If the catalyst composition is used in a fixed bed processes, the sulfidation is preferably carried out subsequent to the shaping step and, if applied, subsequent to the last calcination step. Preferably, the sulfidation is carried out *ex situ*, i.e., the sulfidation is carried out in a separate reactor prior to loading the sulfided catalyst composition into the hydroprocessing unit. Furthermore, it is preferred that the catalyst composition is both sulfided *ex situ* and *in situ*.

Catalyst Compositions of this Invention

The present invention further refers to catalyst compositions obtainable by any of the above-described processes. Furthermore, the present invention pertains to a catalyst composition comprising bulk catalyst particles wherein the bulk catalyst particles comprise 30 - 100 wt.% of at least one Group VIII non-noble metal and at least one Group VIB metal, based on the total weight of the bulk catalyst particles, calculated as metal oxides and wherein the bulk catalyst particles have a surface area of at least 10 m²/g.

Catalyst compositions comprising bulk catalyst particles comprising one Group VIII non-noble metal and two Group VIB metals are preferred. It has been

found that in this case, the bulk catalyst particles are sintering-resistant. Thus the active surface area of the bulk catalyst particles is maintained during use. The molar ratio of Group VIB to Group VIII non-noble metals ranges generally from 10:1 - 1:10 and preferably from 3:1 - 1:3. In the case of a core-shell structured particle, these ratios of course apply to the metals contained in the shell. If more than one Group VIB metal is contained in the bulk catalyst particles, the ratio of the different Group VIB metals is generally not critical. The same holds when more than one Group VIII non-noble metal is applied. In the case where molybdenum and tungsten are present as Group VIB metals, the molybdenum:tungsten ratio preferably lies in the range of 9:1 - 1:9. Preferably the Group VIII non-noble metal comprises nickel and/or cobalt. It is further preferred that the Group VIB metal comprises a combination of molybdenum and tungsten. Preferably, combinations of nickel/molybdenum/tungsten and cobalt/molybdenum/tungsten and nickel/cobalt/molybdenum/tungsten are used. These types of precipitates appear to be sinter-resistant. Thus, the active surface area of the precipitate is remained during use.

The metals are preferably present as oxidic compounds of the corresponding metals, or if the catalyst composition has been sulfided, sulfidic compounds of the corresponding metals.

In the following the bulk catalyst particles (in the following designated as "particles") which are present in the catalyst composition of the present invention will be described in more detail:

Preferably the particles have a surface area of at least 50 m²/g and more preferably of at least 100 m²/g measured VIB the B.E.T. method. It is furthermore preferred that the particles comprise 50 - 100 wt.%, and even more preferably 70 - 100 wt.% of at least one Group VIII non-noble metal and at least

one Group VIB metal, based on the total weight of the particles, calculated as metal oxides. The amount of Group VIB and Group VIII non-noble metals can easily be determined VIB TEM-EDX.

It is desired that the pore size distribution of the particles is approximately the same as the one of conventional hydrotreating catalysts. More in particular, these particles have preferably a pore volume of 0.05 - 5 ml/g, more preferably of 0.1 - 4 ml/g, still more preferably of 0.1 - 3 ml/g and most preferably 0.1 - 2 ml/g determined by nitrogen adsorption. Preferably, pores smaller than 1 nm are not present. Furthermore these particles preferably have a median diameter of at least 50 nm, more preferably at least 100 nm, and preferably not more than 5000 μm and more preferably not more than 3000 μm . Even more preferably, the median particle diameter lies in the range of 0.1 - 50 μm and most preferably in the range of 0.5 - 50 μm .

It was found that the bulk catalyst particles have a characteristic X-ray diffraction pattern which differs from catalysts obtained by co-mixing and conventional hydroprocessing catalysts obtained by impregnation. The X-ray diffraction pattern of the bulk catalyst particles comprises, and preferably essentially consists of, peaks characteristic to the reacted metal components. If, e.g., nickel hydroxy-carbonate has been contacted with a molybdenum and tungsten component as described above, the resulting bulk catalyst particles are characterized by an X-ray diffraction pattern which comprises peaks at d values of (4.09), 2.83, 2.54, 2.32, 2.23, 1.71, (1.54), 1.47. Values in brackets indicate that the corresponding peaks are rather broad and/or have a low intensity or are not distinguished at all. The term "the X-ray diffraction pattern essentially consists of " these peaks means that apart from these peaks, there are essentially no further peaks contained in the diffraction pattern. The precipitate for catalyst

obtained by the solution route has a characteristic X-ray diffraction pattern which differs from catalyst obtained by co-mixing and conventional hydroprocessing catalysts obtained by impregnation. For instance the X-ray diffraction pattern of a Ni-Mo-W precipitate as prepared by the solution route has peaks at d values of 2.52, 1.72 and 1.46.

Generally, it is possible to perform the above-described process in such a way to obtain bulk catalyst particles characterized by an X-ray diffraction pattern that does contain virtually no peak characteristic to the metal components applied in this process as starting materials. Of course, if desired, it is also possible to choose the amounts of metal components in such a way as to obtain bulk catalyst particles characterized by an X-ray diffraction pattern still comprising one or more peaks characteristic to at least one of these metal components. If, e.g., a high amount of the metal component which is at least partly in the solid state during contacting is added, or if this metal component is added in the form of large particles, small amounts of this metal component may be traced in the X-ray diffraction pattern of the resulting bulk catalyst particles.

Generally, if the solid route is applied, at least one of the metals is anisotropically distributed in the particles. The metal of the metal component that is at least partly in the solid state during the solid route is generally concentrated in the inner part, i.e., the core of the final particles. Generally, the concentration of this metal in the outer part, i.e. the shell of the particle is at most 95% and in most cases at most 90% of the concentration of this metal in the core of the particles. Further, it has been found that the metal of a metal component that is applied in the solute state during the solid route is also anisotropically distributed in the particles. More in particular, the concentration of this metal in the core of the particles is generally lower than the concentration of this metal in the shell. Still more in particular, the concentration of this metal in the core of

the particles is at most 80% and frequently at most 65% and often at most 50% of the concentration of this metal in the shell. It must be noted that the above-described anisotropic metal distributions can be found in the composition of the invention, independently upon whether the composition has been calcined or not and/or sulfided.

In the above cases, the shell has generally a thickness of 50 - 1000 nm and preferably of 100 - 500 nm. The amount of these particles in the catalyst composition of the invention preferably lies in the range of 5 - 100 wt.%, based on the total weight of the catalyst composition.

As previously been mentioned, the catalyst composition comprises additionally a suitable binder material. Suitable binder materials are preferably those described above. The particles are embedded in the binder material that functions as glue to hold the particles together. Preferably, the particles are homogeneously distributed within the binder. The presence of the binder thus leads generally to an increased mechanical strength of the final catalyst composition. Generally, the catalyst composition of the invention has a mechanical strength, expressed as side crush strength of at least 1 lb./mm and preferably of at least 3 lb./mm (measured at extrudates with a diameter of 1 - 2 mm). The binder material generally contains 0 - 90 wt.% of the Group VIB and Group VIII non-noble metals which are also contained in the particles. The binder material generally even contains these metals if it has not been composited with any of these metals prior to being combined with the bulk catalyst composition of step (i).

The amount of binder depends on the desired activity of the catalyst composition. Binder amounts from 0 - 95 wt.% of the total composition can be suitable, depending on the envisaged catalytic application. However, to take advantage of

the unusual high activity of the composition of the present invention, binder amounts are generally in the range of 0.5 - 75 wt.% of the total composition.

If desired, the catalyst composition may comprise a suitable cracking component. Suitable cracking components are preferably those described above. The amount of the cracking component is preferably in the range of 0 - 80 wt.%, based on the total weight of the catalyst composition.

Also as previously stated, the catalyst composition may comprise conventional hydroprocessing catalysts. The binder materials and cracking components of the conventional hydroprocessing catalyst generally comprise any of the above-described binder materials and cracking components. The hydrogenation metals of the conventional hydroprocessing catalyst generally comprise Group VIB and Group VIII non-noble metals such as combinations of nickel or cobalt with molybdenum or tungsten. Suitable conventional hydroprocessing catalysts are, e.g., hydrotreating catalysts. These catalysts can be in the spent, regenerated, or fresh state.

Furthermore, the catalyst composition may comprise any compound that is conventionally present in hydroprocessing catalysts such as phosphorus compounds, additional transition metals, rare earth metals, or mixtures thereof. Suitable additional transition metals are, e.g. rhenium, ruthenium, rhodium, iridium, chromium, vanadium, iron, cobalt, platinum, palladium, cobalt, nickel, molybdenum, or tungsten. All these metal compounds generally are present in the oxidic form if the catalyst composition has been calcined and/or in the sulfided form if the catalyst composition has been sulfided.

The surface area of the catalyst composition preferably is at least 40 m²/g, more preferably at least 80 m²/g and most preferably at least 120 m²/g. The total pore

volume of the catalyst composition is preferably at least 0.05 ml/g and more preferably at least 0.1 ml/g as determined by water porosimetry. To obtain catalyst compositions with high mechanical strength, it may be desirable that the catalyst composition of the invention has a low macroporosity.

Characterization methods

1. Side crush strength determination

First, the length of, e.g., an extrudate particle is measured, and then the extrudate particle is subjected to compressive loading by a movable piston. The force required to crush the particle is measured. The procedure is repeated with at least 40 extrudate particles and the average is calculated as force (lbs.) per unit length (mm).

2. Water porosimetry

The pore volume of a sample is determined by filling the pore space to saturation with water. The quantity of water is determined by its volume added or the weight increase of the sample. The pores space can be filled by incrementally adding water from a burette to the sample, with vigorous shaking after each addition, until the first sign of wetness at the outside of the sample appears. Another possibility is to saturate the sample contained in a tube fitted with a porous bottom with water in an ultrasound bath. The excess water (the water not residing in the pores) is removed by centrifugation and the difference in the dry and saturated catalyst weights is then used to determine the total water uptake. From this, the pore volume is calculated.

3. Determination of the loss on ignition (LOI)

A sample is mixed well to prevent inhomogeneity. The weighed and mixed sample is transferred to a preheated and weighed crucible. The crucible is then

put in a drying oven or cold muffle furnace and the temperature is increased. The sample is dried or ignited at this temperature for one hour. The crucible containing the dried or ignited sample is cooled in a desiccator and weighed again.

The LOI is determined according to the following formula

$$\%LOI = \frac{(b-c)}{a} \times 100$$

where a is weight of the sample (in gram), b is the mass of the crucible and the sample before drying and/or ignition (in gram), and c is the weight of the crucible and the sample after drying and/or ignition (in gram).

In the process according to the present invention, a Group VIII non-noble metal-containing compound in solution and a Group VIB metal-containing compound in solution are reacted. Thus, the metal compounds are in the solute state when reacted to obtain a precipitate. The Group VIII non-noble metal-containing compound and the Group VIB metal-containing compound may be in solution when added to the reaction mixture or else will become dissolved when present in the reaction mixture. In the latter case, the metals are actively dissolved in the reaction mixture, for instance by stirring, increasing the amount of solvent, changing the temperature, changing the pressure, or changing the pH. The metals may be dissolved in any protic liquid such as water, carboxylic acids, lower alcohols such as ethanol, propanol, etc., or mixtures thereof. Of course, a protic liquid must be chosen which does not interfere with the precipitation reaction.

If soluble salts are added as such, they will dissolve in the reaction mixture. They will subsequently be precipitated with the Group VIB metal. Within the context of this description soluble means soluble in the solvent at the temperature and pH of the reaction mixture. Suitable nickel, iron and cobalt salts which are soluble in water are nitrates, hydrated nitrates, chlorides, hydrated chlorides sulfates, hydrated sulfates, heteropolyanion compounds of Ni-Mo-W (soluble in boiling water), heteropoly anion compounds of Co-Mo-W (soluble in boiling water). It is also possible to add Group VIII non-noble metal-containing compounds which are not in solution at the time of addition, but where solution is effected in the reaction mixture. Examples of these compounds are metal compounds which contain so much crystal water that upon temperature increase the metal compound will dissolve in its own crystal water. Further, non-soluble metal salts may be added in suspension or as such and solution is effected in the reaction mixture. Suitable non-soluble metal salts are heteropolyanion compounds of Co-Mo-W (moderately soluble in cold water), heteropolyanion compounds of Ni-Mo-W (moderately soluble in cold water).

Suitable Group VIB metals are chromium, molybdenum, tungsten, or mixtures thereof. Suitable chromium, molybdenum, and tungsten compounds are soluble chromium, molybdenum, and tungsten salts. Said salts can be added to the reaction mixture in solution, wetted, or as such. If soluble salts are added as such, they will dissolve in the reaction mixture. They will subsequently be precipitated with the Group VIII non-noble metal. Suitable Group VIB metal salts which are soluble in water are ammonium salts such as ammonium dimolybdate, ammonium tri-, tetra- hepta-, octa-, and tetradeca- molybdate, ammonium para-, meta-, hexa-, and polytungstate, alkali metal salts, silicic acid salts of Group VIB metals such as molybdic silicic acid, molybdic silicic tungstic acid, tungstic acid, metatungstic acid, pertungstic acid, heteropolyanion compounds of Mo-P, Mo-Si, W-P, and W-Si. It is also possible to add Group

VIB metal-containing compounds which are not in solution at the time of addition, but where solution is effected in the reaction mixture. Examples of these compounds are metal compounds which contain so much crystal water that upon temperature increase they will dissolve in their own metal water. Further, non-soluble metal salts may be added in suspension or as such, and solution is effected in the reaction mixture. Suitable non-soluble metals salts are heteropolyanion compounds of Co-Mo-W (moderately soluble in cold water), heteropolyanion compounds of Ni-Mo-W (moderately soluble in cold water).

As will be clear from the above, it is possible to add the Group VIII non-noble metal containing compound and the Group VIB metal-containing compound in various ways, at various temperatures and pHs, in solution, in suspension, and as such, simultaneously and sequentially. Five precipitation methods will be described in more detail:

1. Simultaneous precipitation at a constant pH, in which process a Group VIII non-noble metal-containing acid salt compound is added slowly to a reaction vessel containing a protic liquid which is kept at a constant temperature, with the pH being kept constant by adding a base containing Group VIB metal-containing compound solution. The pH is set such that (at the chosen reaction temperature) precipitation occurs. The Group VIII metal-containing compound is added in solution or as such. It was found that the precipitate prepared by this method had a relatively large particle size depending on the dosing speed (with low dosing speed larger than 10 μm (as measured in the slurry with near forward scattering (Malvern)) and a large surface area of 100 m^2/g or more.
2. Simultaneous precipitation, in which process both the Group VIII non-noble metal-containing compound and the Group VIB metal-containing

compound are added slowly and simultaneously to a reaction vessel containing protic liquid and a compound which decomposes upon temperature increase and thereby increases or decreases the pH. The temperature of the reaction vessel is kept at the decomposition temperature of said compound. In this case precipitation is effected by pH change, and the pH at the beginning of the reaction differs from the final pH after precipitation. It was found that the precipitation obtained with this method had a relatively large particle size (larger than 15 μm).

3. Precipitation, in which process the Group VIII non-noble metal-containing compound is added slowly to a reaction vessel containing Group VIB metal-containing compound dissolved in protic liquid (*or vice versa*) and a compound which decomposes upon temperature increase and thereby increases or decreases the pH. The temperature of the reaction vessel is kept at the decomposition temperature of said compound. In this case precipitation is effected by pH change, and the pH at the beginning of the reaction differs from the final pH after precipitation. It was found that the precipitate obtained with this method had a relatively small particle size (between 1 and 10 μm). It was further found that the amount of Group VIB metal compound which actually ended up in the precipitate was larger than in any of the other precipitation methods described above.
4. Precipitation at a constant pH, in which process the Group VIII non-noble metal-containing compounds is added slowly to a reaction vessel containing Group VIB metal-containing compound dissolved in protic liquid or *vice versa*. The pH is kept such that (at the chosen reaction temperature) precipitation occurs by adding acid or base to the reaction vessel.

5. Solution of the metal compounds in their own crystal water with subsequent evaporation of the water so that precipitation occurs. In this method the Group VIII non-noble metal-containing compound and the Group VIB metal-containing compound are mixed in a reaction vessel and heated. After solution of the metals the water is evaporated, optionally under vacuum, to effect precipitation.

One embodiment of the present invention pertains to a process for the preparation of a catalyst composition comprising a Group VIII non-noble metal and a Group VIB metal wherein a Group VIII non-noble metal-containing compound in solution and a Group VIB metal-containing compound in solution are reacted in a reaction mixture to obtain a precipitate, with the proviso that the precipitate is not nickel molybdate in which at least a portion but less than all of the molybdenum is replaced by tungsten.

Subsequently to precipitation, the precipitate may be isolated from the liquid and dried. All conventional isolation methods such as filtration, centrifugation, decantation may be used. Also all conventional drying methods are suitable such as oven drying, spray-drying, etc. The precipitate can also be dried at room temperature.

Optionally, the precipitate is thermally treated in oxygen-containing atmosphere such as air, steam, in steam and oxygen-containing atmosphere or in inert atmosphere. Said thermal treatment is conducted at a temperature between 100-600°C, preferably between 350°-500°C.

In a further embodiment of the solution method of the present invention a filler is added to the reaction mixture and/or precipitate. Fillers may be added to the catalyst composition to dilute the catalyst when it is too active or to adjust the

density. These fillers can be added either in suspension or as such at any stage of the process and combined with any other component added. Suitable fillers include used hydroprocessing catalyst, regenerated hydroprocessing catalysts, fresh hydroprocessing catalyst, clay, and mixtures thereof.

The precursor compound can also be readily prepared by one of several methods, including a variation of the boiling decomposition method used by Teichner and Astier in which a tungsten compound is added to the initial mixture of a molybdenum salt, a nickel salt and ammonium hydroxide. Direct precipitation and pH controlled precipitation may also be used to prepare the precursor compound. In all cases, however, water soluble salts of nickel, molybdenum and tungsten are employed.

Preferably, the molybdenum and tungsten salts are ammonium compounds, e.g., ammonium molybdate, ammonium metatungstate, while the nickel salt may be the nitrate or hydrated nitrates.

In the boiling decomposition method, the salts are dissolved in water to make an acidic solution, after which additional NH_4OH is added to make a basic solution. The solution is then heated to boiling to drive off ammonia and form a precipitate which is filtered and dried, e.g. at 100-125°C.

In the direct precipitation method, initially the molybdate and tungstate salts are dissolved in water, NH_4OH is added to form a basic solution, and the solution is warmed. A warm, e.g., 90°C, nickel salt solution (aqueous) is slowly added to the initial solution, a precipitate is formed, the solution is hot filtered and dried. In either the boiling decomposition method or the direct precipitation method, washing of the filtrate is minimized to prevent leaching.

In general, all of the components, the Ni, Mo, W, NH_3 , are mixed in solution together and heated to a $\text{pH} < 7$ to form the precipitate, i.e., the precursor compound. This may be accomplished by either of two methods: (1): adding all of the components together with an excess of ammonia to dissolve the components and then heating to drive off the ammonia such that the $\text{pH} < 7$ (heating may be at less than 100°C , preferably about $50\text{-}90^\circ\text{C}$); or (2) adding together one or more separate solutions of each component such that the final pH is < 7 ; in each case recovering the resulting precipitate.

In another embodiment, a binder can be added to the bulk mixed metal oxide to maintain particle integrity. The binder can be silica, alumina, silica-alumina or other materials generally known as particle binders. When utilizing a binder, the amount may range from about 1-30 wt% of the finished catalyst, preferably about 5-26 wt% of the finished catalyst.

After recovering the precursor product, regardless of preparation method, the precursor is decomposed at temperatures ranging from about $300\text{-}450^\circ\text{C}$ in a suitably inert or air atmosphere.

The decomposed precursor can be sulfided or pre-sulfided by a variety of known methods. For example, the decomposition product can be contacted with a gas comprising H_2S and hydrogen, e.g., 10% $\text{H}_2\text{S}/\text{H}_2$, at elevated temperatures for a period of time sufficient to sulfide the decomposition product, usually at the point of H_2S breakthrough in the exit gas. Sulfiding can also be effected, in situ, by passing a typical feedstock containing sulfur over the decomposition product.

Any hydrocarbon containing feed which also contains nitrogen may be treated with the enhanced catalysts of this invention. Thus, the HDN process with these catalysts may range from petroleum distillates to residual stocks,

either virgin or cracked, to synthetic fuels such as coal oils or shale oils. The HDN process is particularly useful with feeds containing high levels of nitrogen, e.g., at least about 500 wppm total nitrogen compounds. Nitrogen removal is at least about 50%, preferably at least about 80%.

Process conditions applicable for the use of the catalysts described herein may vary widely depending on the feedstock to be treated. Thus, as the boiling point of the feed increases, the severity of the conditions will also increase. The following table serves to illustrate typical conditions for a range of feeds.

FEED	TYPICAL BOILING RANGE °C	TEMP. °C	PRESS, BAR	SPACE VELOCITY V/V/HR	H ₂ GAS RATE SCF/B
naphtha	25-210	100-370	10-60	0.5-10	100-2,000
diesel	170-350	200-400	15-110	0.5-4	500-6,000
heavy gas oil	325-475	260-430	15-170	0.3-2	1000-6,000
lube oil	290-550	200-450	6-210	0.2-5	100-10,000
residuum	10-50%>575	340-450	65-1100	0.1-1	2,000-10,000

While the invention described herein shows enhanced activity for hydrodenitrogenation, most HDN catalysts will also show hydrodesulfurization (HDS) activity. Consequently, the catalysts and processes described herein will be useful on feeds containing both nitrogen and sulfur, and will be particularly useful on feeds high in nitrogen.

The following examples will serve to illustrate, but not limit, this invention.

Example 1. Preparation of NH₄-Ni-Mo-O Phase (boiling decomposition as per Teichner and Astier procedure):

In a 1 liter flask, 26.5 g ammonium molybdate (0.15 moles Mo) and 43.6 g nickel nitrate hexahydrate (0.15 moles Ni) were dissolved in 300 cc of water so that the resulting pH equaled 4.3. To this solution, a concentrated NH_4OH solution was added. At first, a precipitate formed which on further addition of NH_4OH dissolved to give a clear blue solution with a pH of 8.3, and additional NH_4OH (~250cc) was added until a pH of 10 was reached. The solution was heated to 90°C for 3 h during which ammonia gas evolved and a green precipitate formed. The final pH lay between 6.8 and 7. The suspension was cooled to room temperature, filtered, washed with water and dried at 120°C overnight. About 18.6g of material was obtained. The sample analyzed for Ni at 26.6 wt.% and Mo at 34 wt.%. The X-ray diffraction spectra of the phase matches the pattern reported by Teichner.

Example 2. Preparation of $\text{NH}_4\text{-Ni-Mo}_5\text{W}_5\text{-O}$ by boiling decomposition:

In a 1 liter flask, 13.2 g ammonium molybdate (0.075 moles Mo), 18.7 g ammonium metatungstate (.075 moles W) and 43.6 g nickel nitrate hexahydrate (0.15 moles Ni) were dissolved in 300cc of water so that the resulting pH equaled 4.3. To this solution, a concentrated NH_4OH solution (~600cc) was added until the pH reached 10. At this point, some precipitate remained. The solution was refluxed at ~100°C for 3 h. During this heating, the precipitate dissolved to give a clear blue solution and on further heating, a green precipitate formed. The heating was continued until the pH reached between 6.8 and 7. The suspension was cooled to room temperature, filtered, washed with water and dried at 120°C overnight. 18 grams of material is obtained. The X-ray diffraction spectra of the phase is given in Figure 2 showing an amorphous background with the two largest peaks at $d=2.58$ and $1.70\text{\AA}$.

Example 3. Preparation of $\text{NH}_4\text{-Ni-Mo}_{.5}\text{W}_{.5}\text{-O}$ by direct precipitation:

In a 1 liter flask, 17.65 g of ammonium molybdate (0.1 mole Mo) and 24.60 g of ammonium metatungstate (0.1 mole W) were dissolved in 800 cc of water giving a solution pH of ~5.2. To this solution 0.4 moles of NH_4OH (~30 cc) was added, raising the pH to ~9.8 (solution A). This solution was warmed to 90°C. A second solution was prepared by adding 58.2 g of nickel nitrate, (0.2 moles Ni) which was dissolved in 50 cc of water (solution B) and maintained at 90°C. This solution was added dropwise at a rate of 7 cc/min into the ammonium molybdate/ammonium metatungstate solution. A precipitate begins to form after 1/4 of the solution was added. This suspension which was at a pH ~6.5 was stirred for 30 minutes while the temperature was maintained at 90°C. The material was filtered hot, washed with hot water, and dried at 120°C. Approximately 38 g of material was recovered.

Example 4. Preparation of $\text{NH}_4\text{-Ni-Mo}_{.5}\text{-Mo}_{.5}\text{W}_{.5}\text{-O}$ by controlled pH precipitation:

Two solutions were prepared with the same amounts of nickel, tungsten, molybdenum and ammonium hydroxide are described in Example 3 (solutions A and B) except that each solution contained about 700 cc of water. The two solutions were added into a separate vessel initially containing 400 cc of water held at 90°C. Solution B (the acidic solution) was pumped into the vessel at a constant rate of ~15cc/min, while solution A is added through a separate pump which is under feedback PC control and set to maintain the pH at 6.5. On mixing the two solutions a precipitate forms. The slurry was stirred at 90°C for 30 minutes, filtered hot, washed with hot water, and dried at 120°C.

Example 5. Catalytic Evaluation Using Dibenzothiophene (DBT):

1.5-2 g of the catalysts of Examples 1-4 were placed in a quartz boat which was in turn inserted into a horizontal quartz tube and placed into a Lindberg furnace. The temperature was raised to 370°C in about one hour with N₂ flowing at 50 cc/m, and the flow continued for 1.5 h at 370°C. N₂ was switched off and 10% H₂S/H₂ then added to the reactor at 20 cc/m, the temperature increased to 400°C, and held there for 2 hours. The heat was then shut off and the catalyst cooled in flowing H₂S/H₂ to 70°C, at which point this flow was discontinued and N₂ was added. At room temperature, the quartz tube was removed and the material transferred into a N₂ purged glove box. Catalysts were evaluated in a 300cc modified Carberry batch reactor designed for constant hydrogen flow. The catalyst was pilled and sized to 20/40 mesh and one gram was loaded into a stainless steel basket, sandwiched between a layer of mullite beads. 100 cc of liquid feed, containing 5 wt% dibenzothiophene in decalin was added to the autoclave. A hydrogen flow of 100 cc/min was passed through the reactor and the pressure was maintained at 3150kPa using a back pressure regulator. The temperature was raised to 350°C at 5-6 deg/min and run until either 50% DBT was converted or until 7 hours was reached. A small aliquot of product was removed every 30 minutes and analyzed by GC. Rate constants for the overall conversion as well as the conversion to the reaction products biphenyl (BP) and cyclohexylbenzene (CHB) were calculated as described by M. Daage and R. R. Chianelli [J. Cat. 149, 414-27 (1994)] and are shown in Table 1. As described in that article, high selectivities to cyclohexylbenzene relative to BP during the desulfurization reaction are a good indication of a catalyst with high hydrodenitrogenation activity, whereas high selectivities of BP relative to CHB indicates a catalyst with high hydrodesulfurization activity.

The results show that partial substitution of tungsten for molybdenum results in catalysts that are substantially higher for DBT conversion. A standard supported

Ni-Mo on Al₂O₃ catalyst is also shown for comparison. The high CHB/BP ratio suggests that the catalysts are active for HDN.

Table 1. Comparison of Activity in DBT Conversion Tests With Tungsten Addition by Different Preparation Schemes

Catalyst	Preparation technique	Example #	K _{total} @ 350°C	CHB/BP @ 350°C
NH ₄ -Ni-Mo-O	boiling decomposition	1	106	10.4
NH ₄ -Ni-Mo ₅ W ₅ -O	boiling decomposition	2	171	10.2
NH ₄ -Ni-Mo ₅ W ₅ -O	direct precipitation	3	167	12.4
NH ₄ -Ni-Mo ₅ W ₅ -O	controlled pH preparation	4	181	12.0
Ni ₁ Mo/Al ₂ O ₃	impregnation		129	6.4

Example 6.

A series of catalysts were prepared in accordance with the general preparation scheme of example 2 (i.e., boiling decomposition) but varying the Mo and W relative ratios by changing the amount of ammonium molybdate and ammonium metatungstate added to the solutions. Decomposition was effected as described in Example 5. The catalysts so prepared are shown in Table 2 along with their catalytic activities for DBT measured as described in Example 5.

Table 2. Comparison of Activity in DBT Conversion Tests with Variation in Relative W and Mo content

Catalyst	Sample	Ammonium molybdate (g)	Ammonium metatungstate (g)	Nickel nitrate hexahydrate (g)	K _{total} @ 350°C	CHB/BP @ 350°C
NH ₄ -NiW-O	18983-97	0	36.95	43.62	128	11.3
NH ₄ -NiMo ₉ W ₁ -O	18983-92	23.83	3.69	43.62	141	10.5

NH ₄ - NiMo ₇ W ₃ -O	18983-95	18.54	11.09	43.62	158	11.5
NH ₄ - NiMo ₅ W ₅ -O	18357-109	13.17	18.74	43.62	171	10.2
NH ₄ - NiMo ₃ W ₇ -O	18983-101	7.94	25.87	43.62	154	11.6
NH ₄ - NiMo ₁ W ₉ -O	18983-125	2.65	33.62	43.62	132	14.1

The data show that the most active catalyst contains an approximately equimolar mixture of tungsten and molybdenum.

Example 7.

A series of catalysts were prepared as described in Example 3 (direct precipitation) in which equimolar mixtures of Mo and W were precipitated but the nickel content was varied. Decomposition was effected as described in Example 5. The catalysts so prepared are shown in Table 3 along with their catalytic activities for DBT measured as described in example 5.

Table 3. Variation of Nickel Content in NH₄-Ni-Mo₅W₅-O Catalysts

Catalyst	Sample	Ammonium molybdate (g)	Ammonium metatungstate (g)	Nickel nitrate hexahydrate (g)	K _{tota} l @ 350°C	CHB/BP @ 350°C
NH ₄ - Ni _{0.75} Mo ₅ W ₅ -O	19086- 110	17.65	24.6	43.65	171	13.0

NH ₄ - Ni _{1.0} Mo ₅ W ₅ -O	19086-82	17.65	24.6	58.2	167	12.4
NH ₄ - Ni _{1.25} Mo ₅ W ₅ -O	19086- 111	17.65	24.6	72.75	174	11.0
NH ₄ - Ni _{1.5} Mo ₅ W ₅ -O	19086- 112	17.65	24.6	87.3	148	9.55

Catalytic performance does not change substantially with variations in Ni from 0.75 to 1.5, although K appears to go through a maximum at about 1.25 Ni.

Example 8. A series of catalysts were prepared in which the quantity of NH₄OH used in the preparation was varied. The catalysts were prepared in accordance to the procedure described in Example 3 except that the amount of NH₄OH in solution A was varied to change to NH₄OH/Ni molar ratio when the two solutions were mixed. Decomposition was effected as described in Example 5. The catalysts so prepared are shown in Table 4 along with their catalytic activities for DBT measured as described in Example 5.

Table 4. Variation in NH₄OH Addition to Preparation

Catalyst NH ₄ OH/Ni mole ratio	Sample	Ammonium molybdate (g)	Ammonium metatungstate (g)	Nickel nitrate hexahydrate (g)	cm ³ conc NH ₄ OH	K _{total} l @ 350°C	K _{CHB} /BP @ 350°C
1:2	19086-96	17.65	24.6	43.65	6.8	102	10.5
1:1	19086-97	17.65	24.6	58.2	14	137	10.4
2:1	19086-82	17.65	24.6	72.75	30	167	12.4

3:1	19086-104	17.65	24.6	87.3	41	164	11.4
4:1	19086-106	17.65	24.6	87.3	55	161	12.1

While decomposition of the precursor compound will drive off most, if not all, of the ammonium portion of the precursor, the preparation of the precursor and the catalytic utility of the decomposition product can be affected by the amount of NH_4OH employed. Thus, the effectiveness of the decomposition product as a catalyst is enhanced when the $\text{NH}_4\text{OH}/\text{Ni}$ ratio in the preparation of the precursor compound is from about 1:1 to about 4:1, preferably about 1.5:1 to about 4:1, and more preferably about 2:1 to about 4:1. While not wishing to be bound by any particular theory or mechanism, there is some evidence the $\text{NH}_4\text{OH}/\text{Ni}$ ratio causes the Ni-M-W-O phase to change in the decomposition product.

Example 9. The catalysts of examples 1 and 2 were compared against standard supported Ni-Mo catalysts for the conversion of a LSADO (low sulfur auto diesel oil feed). This feed contained 510 wppm sulfur, 50 wppm nitrogen, and 30.6% aromatics with a gravity of 39.8° API. The catalysts were tested at 579°F, 650 psig of H_2 , and 1850 SCFB/B of H_2 . The relative activities of the different catalysts are summarized in Table 5.

Table 5. Relative Hydrotreating Activities on LSADO Feed

Catalyst	Relative Volumetric HDS Activity	Relative Volumetric HDN Activity
$\text{Ni}_2\text{Mo}/\text{Al}_2\text{O}_3$	1	1
$\text{NH}_4\text{-NiMo-O}$	0.25	0.50
$\text{NH}_4\text{-Ni}_{1.0}\text{Mo}_{0.5}\text{W}_{0.5}\text{-O}$	1.4	2.05

The Ni, Mo/Al₂O₃ catalyst is a standard HDN/HDS catalyst, the NH₄-Ni-Mo phase is the bulk phase with no tungsten, and the NH₄-Ni_{1.0}Mo_{0.5}W_{0.5}-O is the bulk phase with partial substitution of W for Mo. The NH₄-NiMo-O catalyst is also representative of known compounds. The catalyst of this invention is illustrated by NH₄-Ni_{1.0}Mo_{0.5}W_{0.5}-O and the data show the clear advantage of ammonium nickel tungsten molybdate for HDN activity.

Example 10. Preparation of a bulk catalyst composition according to the solid route:

18.1kg-ammonium dimolybdate (15.33kg MoO₃) are dissolved in 575 liters water. Subsequently 28.5kg ammonium metatungstate (24.69kg WO₃) is added to the solution. The resulting solution is preheated up to 90°C. 26.5kg NiCO₃ (49.7% Ni) powder is mixed with water and the resulting paste is added to the ammonium dimolybdate/ammonium metatungstate solution. The resulting mixture is reacted for 7 hours at 89°C.

Example 11. Preparation of a bulk catalyst composition according to the solution route:

In a 1-liter flask, 13.2 g ammonium molybdate (0.075 moles Mo), 18.7 g ammonium metatungstate (0.075 moles W) and 43.6 g nickel nitrate hexahydrate (0.15 moles Ni) were dissolved in 300 ml water so that the resulting pH equaled 4.3. To this solution, a concentrated NH₄OH solution (about 600 ml) was added until the pH reached 10. At this point, some precipitate remained. The solution was refluxed at 100°C for 3 hours. During this heating, the precipitate dissolved to give a clear blue solution and on further heating, a green precipitate formed. The heating was continued until the pH reached a value between 6.8 and 7.0. The suspension was cooled to room temperature, filtered, washed with water and dried at 120°C overnight. 18 grams of material were obtained.

Example 12. (sample 2110587)

657g of a Ni-Mo-W bulk catalyst composition obtained according to the procedure described in Examples 10 or 11 was added to 1362 g of an aqueous slurry containing 125g of alumina (prepared by precipitation of sodium aluminate and aluminum sulfate). The resulting Ni-Mo-W bulk catalyst - alumina composition was subsequently mixed at 80°C until an LOI of 31% was obtained. The resulting composition was subsequently extruded and the extrudates were dried at 120.C for about 90 minutes and subsequently calcined at 385°C for one hour in air.

Example 13. (sample 2110598)

The process of Example 12 was repeated except that instead of the alumina suspension, a silica sol containing 10 wt.% silica were applied.

Example 14. (sample 2110591)

657g of a Ni-Mo-W bulk catalyst composition obtained according to the procedure described in Examples 7 or 8 was added to 510g of a boehmite paste containing 125g boehmite. The rebuffing paste was mixed at 60°C to obtain an LOI of 42%. The resulting composition was extruded, dried and calcined as described in Example 12.

Example 15. (sample 2110469)

The procedure described in Example 7 or 8 was repeated except that alumina is present during the preparation of the bulk catalyst composition. To 755g of the resulting dried Ni-Mo-W bulk catalyst - alumina composition containing 60g alumina, 461g water and a small amount of nitric acid were added. The resulting mixture was mixed at 70°C while evaporating water until an LOI of 34% was obtained. The resulting composition was extruded, dried and calcined as described in Example 12.

Example 16.

Ammonium molybdate, ammonium tungsten and/or ammonium chromate are dissolved and combined in a first reactor. The temperature is increased to 90°C. The Group VIII salt is dissolved in a second reactor and heated to 90°C. Ammonium hydroxide is added to the first reactor to form a basic solution. The Group VIII metal solution is added to the first dropwise with stirring in 20 minutes. After 30 minutes, the precipitate is filtered and washed. The precipitate is dried overnight at 120°C and calcined at 385°C.

Example 17.

The precipitation method of Example 16 was used to prepare a precipitate from ammonium dimolybdate, ammonium meta tungstate and $\text{Fe(III)(NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ in 98% yield comprising 41.2 wt.% Fe_2O_3 , 21.3 wt.% MoO_3 , and 36.9 wt.% WO_3 . The surface area of the precipitate was 76 m^2/g . The pore volume as measured up to 60 nm by BET using the adsorption curve was 0.147 ml/g.

Example 18.

The precipitation method of Example 16 was used to prepare a precipitate from $\text{Ni(CO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in 87.7% yield comprising 52.2 wt.% NiO, 29.4 wt.% MoO_3 , and 16.6 wt.% Cr_2O_3 . The surface area of the precipitate was 199 m^2/g . The pore volume as measured up to 60 nm by BET using the adsorption curve was 0.276 ml/g.

Example 19.

The precipitation method of Example 16 was used to prepare a precipitate from $\text{Ni(CO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$, and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in 87.7% yield comprising 44.0 wt.% NiO, 42.4 wt.% WO_3 , and 11.8 wt.% Cr_2O_3 . The surface area of the

precipitate was 199 m²/g. The pore volume as measured up to 60 nm by BET using the adsorption curve was 0.245 ml/g.

Example 20.

A 350N dewaxed oil was processed at hydrotreating conditions in a small scale pilot unit over both a conventional NiMo hydrotreating (HT) catalyst and the bulk metal catalyst. Feed quality, operating conditions and pilot plant test results are given in the table below. The extent of saturation over the bulk metal catalyst is much higher, even at milder operating conditions, than for the conventional HT catalyst. The relative desulfurization activity for the bulk metal catalyst was about 600% higher than the conventional catalyst.

	350N Dewaxed Oil Feed	Conventional NiMo HT Catalyst		Bulk Metal Catalyst	
H ₂ Partial Pressure, psig		2000	2000	2000	2000
H ₂ Treat Gas Rate, SCF/bbl		2500	2500	2500	2500
RX Temp, °C		350	340	300	325
RX LHSV, hr ⁻¹		0.6	1.7	0.6	1.6
Dewaxed 390C+ Product Properties					
UV Absorbance at 274 nm	650	72.5	162	9.2	23.7
Saturates, wt%	76.7	91.7	89.2	93.4	93
Sulfur, wppm	238	0.9	14	1.3	1.2

Example 21.

A 350N dewaxed oil was processed at hydrotreating conditions in a small scale pilot unit over conventional NiMo hydrotreating (HT) catalyst followed by a bulk metal catalyst. H₂S and NH₃ were removed from the treat gas between catalysts. Feed quality, operating conditions and pilot plant test results are given in the table below. Very low levels of sulfur and UV absorbance were achieved.

	350N Dewaxed Oil Feed	R1 Conventional NiMo HT Catalyst	R2 Bulk Metal Catalyst
H2 Partial Pressure , psig		2000	2000
H2 Treat Gas Rate, SCF/bbl		2500	2500
RX Temp, °C		330 to 350	325
RX LHSV, hr-1		0.6 to 2.0	1.8
Dewaxed 390C+ Product Properties			
UV Absorbance at 274 nm	650	93.4	14.5
Saturates, wt%	76.7	91.1	93.3
Sulfur, wppm	238	0.9	0.5

CLAIMS:

1. A process for preparing a lubricating oil basestock containing at least about 90% saturates which comprises:
 - (a) passing a feedstock to a hydrotreating zone containing at least one hydrotreating reactor containing a hydrotreating catalyst:
 - (b) hydrotreating the feedstock in the presence of the hydrotreating catalyst under hydrotreating conditions wherein the hydrotreating catalyst is a bulk metal catalyst comprising non-noble Group VIII metal molybdate in which at least a portion but less than all of molybdenum is replaced by tungsten to produce a hydrotreated feedstock; and
 - (c) fractionating the hydrotreated feedstock.
2. A process for preparing a lubricating oil basestock containing at least about 90% saturates which comprises:
 - (a) passing a feedstock to a first hydrotreating zone containing at least one hydrotreating reactor containing a first non-bulk metal hydrotreating catalyst;
 - (b) hydrotreating the feedstock in the presence of the first hydrotreating catalyst under first hydrotreating conditions wherein the first hydrotreating catalyst comprises at least one Group VIB and at least one non-noble Group VIII metal on a refractory oxide support to produce a first hydrotreated feedstock;

(c) passing at least a portion of the first hydrotreated feedstock to a second hydrotreating zone containing at least one hydrotreating reactor containing a second hydrotreating catalyst;

(d) hydrotreating the first hydrotreated feedstock in the second hydrotreating zone under second hydrotreating conditions wherein the second hydrotreating catalyst in said second hydrotreating zone is a bulk metal catalyst comprising non-noble Group VIII metal molybdate in which at least a portion but less than all of molybdenum is replaced by tungsten to produce a second hydrotreated feedstock;

(e) fractionating the second hydrotreated feedstock.

3. A process for preparing a petroleum oil containing at least about 90% saturates which comprises:

(a) passing a feedstock to a hydrotreating zone containing at least one hydrotreating reactor containing a hydrotreating catalyst;

(b) hydrotreating the feedstock in the presence of the hydrotreating catalyst under hydrotreating conditions wherein the hydrotreating catalyst is a bulk metal catalyst comprising non-noble Group VIII metal molybdate in which at least a portion but less than all of molybdenum is replaced by tungsten to produce a hydrotreated feedstock;

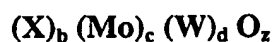
(c) fractionating the hydrotreated feedstock to produce a first basestock;

(d) passing the first basestock to a hydrogenation zone containing at least one hydrogenation reactor containing a hydrogenation catalyst;

(e) hydrogenating the first basestock in the presence of the hydrogenation catalyst under hydrogenation conditions wherein the hydrogenation catalyst comprises at least one Group VIII metal; and

(f) fractionating the hydrogenated product from step (e) to produce a petroleum oil containing at least about 90% saturates.

4. The process of claims 1, 2 or 3 wherein the bulk metal catalyst is represented by the formula:



wherein X is non-noble Group VIII metal, the molar ratio of b: (c+d) is 0.5/1 to 3/1, the molar ratio of c:d is >0.01/1, and $z = [2b + 6(c + d)]/2$.

5. The process of claim 4 wherein the molar ratio of b:(c+d) is 0.75/1 to 1.5/1.

6. The process of claim 5 wherein the molar ratio of b:(c+d) is 0.75/1 to 1.25/1.

7. The process of claim 4 wherein the molar ratio of c:d is >0.1/1.

8. The process of claim 7 wherein the molar ratio of c:d is 1/10 to 10/1.

9. The process of claim 8 wherein the molar ratio of c:d is 1/3 to 3/1.

10. The process of claim 3 wherein the hydrogenation catalyst further contains at least one Group VIB metal.
11. The process of claim 3 wherein the Group VIII metal is a non-noble metal.
12. The process of claim 11 wherein the non-noble metal is nickel.
13. The process of claims 1 or 3 wherein the hydrotreating conditions comprise temperatures of from 250 to 400 °C, hydrogen pressures of from 500 to 3500 psig (3549 to 24234 kPa), liquid hourly space velocities of from 0.1 to 5.0 and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³).
14. The process of claim 2 wherein the first hydrotreating conditions in the first hydrotreating zone comprise temperatures of from 250 to 400 °C, hydrogen pressures of from 500 to 3500 psig (3549 to 24234 kPa), liquid hourly space velocities of from 0.1 to 5.0 and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³), and the second hydrotreating conditions in the second hydrotreating zone comprise temperatures of from 250 to 400 °C, hydrogen pressures of from 500 to 5000 psig (3549 to 24234 kPa), liquid hourly space velocities of from 0.1 to 5.0 and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³).
15. The process of claim 3 wherein the hydrogenation conditions comprise temperatures of from 150 to 400 °C, hydrogen pressures of from 500 to 3500 psig (3549 to 24234 kPa), liquid hourly space velocities of from 0.1 to 5.0 and hydrogen treat gas rates of from 500 to 5000 scf/B (89 to 890 m³/m³).

16. The process of claims 1, 2 or 3 wherein the petroleum oil is a white oil.
17. The process of claim 16 wherein the white oil is a technical or medicinal white oil.
18. The process of claim 4 wherein the non-noble metal is Ni or Co.
19. The process of claim 4 wherein the non-noble metal is Ni.

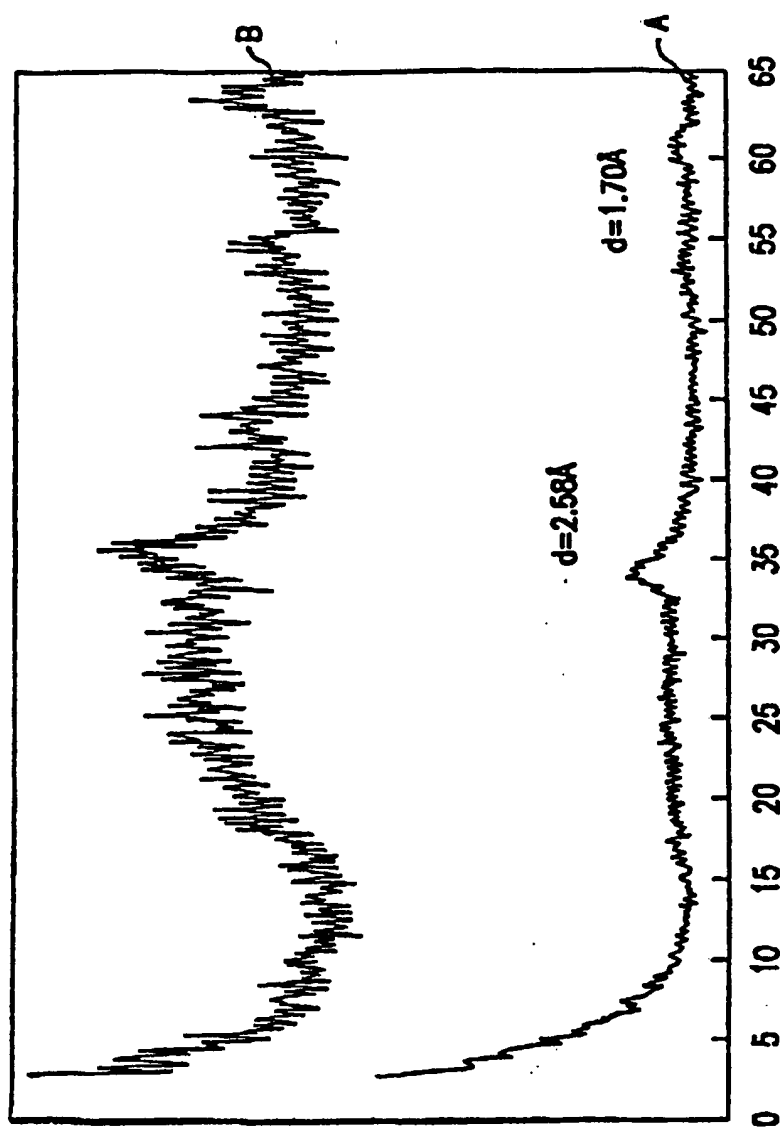


FIG. 1

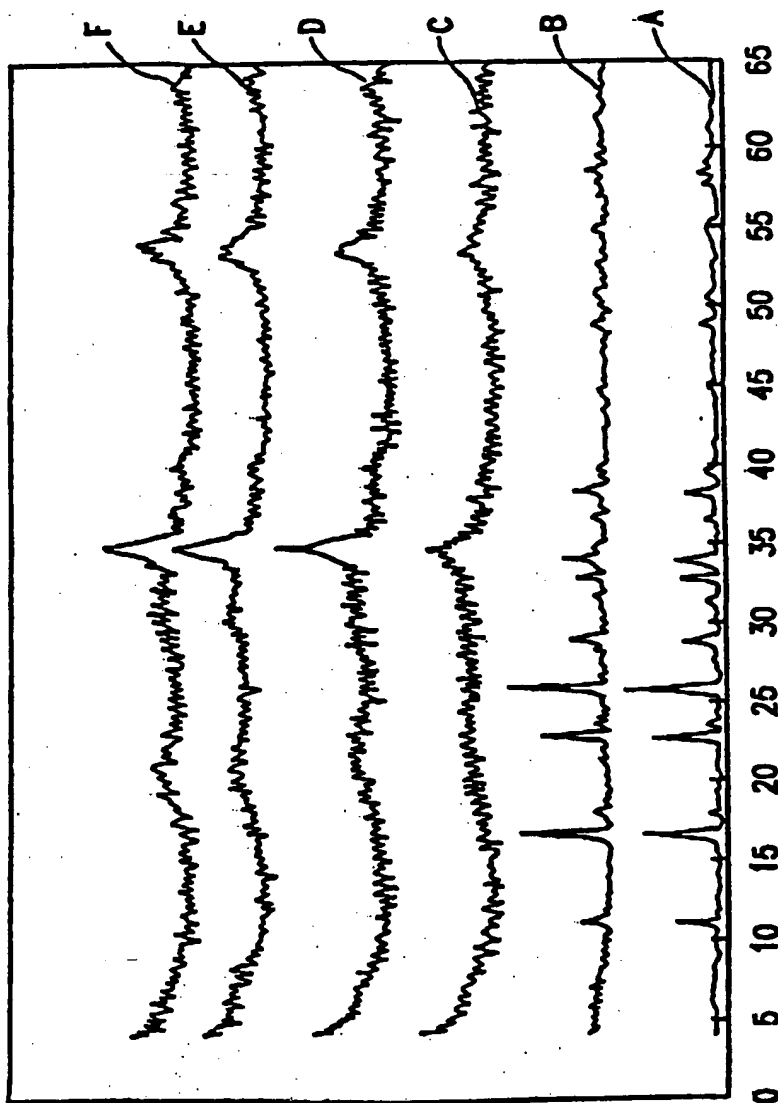


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/01007

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C10G 71/00, 47/02, 47/04, 11/00, 11/02, 11/04

US CL : 208/18, 108, 112,113, 121, 123, 124, 308

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/18, 108, 112,113, 121, 123, 124, 308

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,850,746 A (ROBSON) 26 November 1974, col. 1, line 12 to col. 36, line 66.	1-19
A	US 4,808,563 A (VELENYI) 28 February 1989, col. 3, line 55 to col. 4, line 63.	4-12, 18, 19



Further documents are listed in the continuation of Box C.



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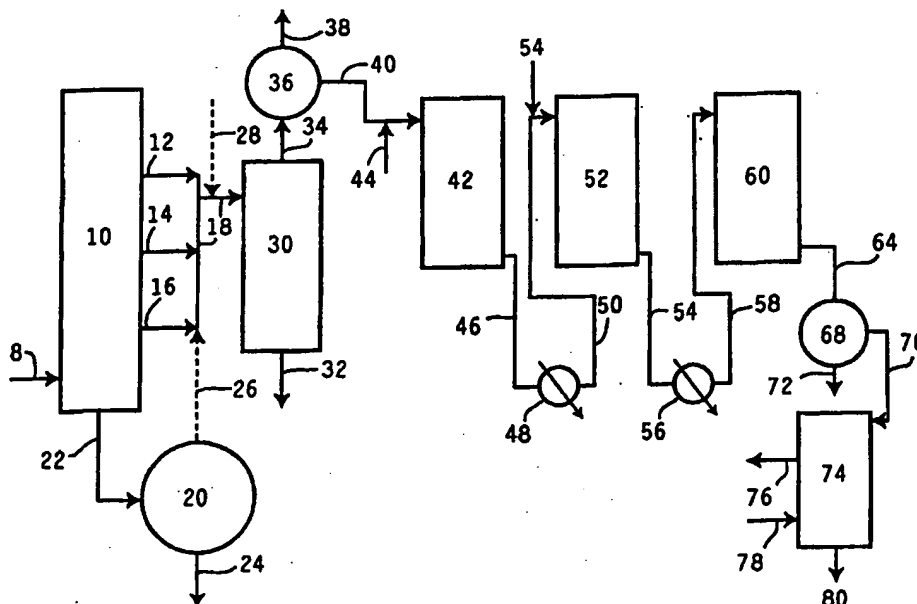
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(21) International Application Number: PCT/US99/03108 (22) International Filing Date: 12 February 1999 (12.02.99) (30) Priority Data: 09/023,573 13 February 1998 (13.02.98) US (71) Applicant: EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US). (72) Inventors: CODY, Ian, A.; 7942C Wrenwood Boulevard, Baton Rouge, LA 70809 (US). BOATE, Douglas, Raymond; 263 Shady Lake Parkway, Baton Rouge, LA 70810 (US). MURPHY, William, John; 16445 Coliseum Avenue, Baton Rouge, LA 70816 (US). LETA, Daniel, Paul; 15 Rustic Trail, Flemington, NJ 08822 (US). (74) Agents: OTT, Roy, J. et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US).		(81) Designated States: AU, CA, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: **HYDROCONVERSION PROCESS FOR MAKING LUBRICATING OIL BASESTOCKS**



(57) Abstract

A process for producing a lubricating oil basestock having at least 90 wt.% saturates and a VI of at least 105 by selectively hydroconverting a raffinate from a solvent extraction zone (20) to a two step hydroconversion through a first hydroconversion unit (42) to a second hydroconversion unit (52) followed by a hydrofinishing zone (60) and a dewaxing zone (74).

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HYDROCONVERSION PROCESS FOR MAKING LUBRICATING OIL BASESTOCKS

FIELD OF THE INVENTION

This invention relates to a process for preparing lubricating oil basestocks having a high saturates content, high viscosity indices and low volatilities.

BACKGROUND OF THE INVENTION

It is well known to produce lubricating oil basestocks by solvent refining. In the conventional process, crude oils are fractionated under atmospheric pressure to produce atmospheric resids which are further fractionated under vacuum. Select distillate fractions are then optionally deasphalted and solvent extracted to produce a paraffin rich raffinate and an aromatics rich extract. The raffinate is then dewaxed to produce a dewaxed oil which is usually hydrofinished to improve stability and remove color bodies.

Solvent refining is a process which selectively isolates components of crude oils having desirable properties for lubricant basestocks. Thus the crude oils used for solvent refining are restricted to those which are highly paraffinic in nature as aromatics tend to have lower viscosity indices (VI), and are therefore less desirable in lubricating oil basestocks. Also, certain types of aromatic compounds can result in unfavorable toxicity characteristics. Solvent refining can produce lubricating oil basestocks have a VI of about 95 in good yields.

Today more severe operating conditions for automobile engines have resulted in demands for basestocks with lower volatilities (while retaining low viscosities) and lower pour points. These improvements can only be achieved with

basestocks of more isoparaffinic character, i.e., those with VI's of 105 or greater. Solvent refining alone cannot economically produce basestocks having a VI of 105 with typical crudes. Nor does solvent refining alone typically produce basestocks with high saturates contents. Two alternative approaches have been developed to produce high quality lubricating oil basestocks; (1) wax isomerization and (2) hydrocracking. Both of the methods involve high capital investments. In some locations wax isomerization economics can be adversely impacted when the raw stock, slack wax, is highly valued. Also, the typically low quality feedstocks used in hydrocracking, and the consequent severe conditions required to achieve the desired viscometric and volatility properties can result in the formation of undesirable (toxic) species. These species are formed in sufficient concentration that a further processing step such as extraction is needed to achieve a non-toxic base stock.

An article by S. Bull and A. Marmin entitled "Lube Oil Manufacture by Severe Hydrotreatment", Proceedings of the Tenth World Petroleum Congress, Volume 4, Developments in Lubrication, PD 19(2), pages 221-228, describes a process wherein the extraction unit in solvent refining is replaced by a hydrotreater.

U.S. Patent 3,691,067 describes a process for producing a medium and high VI oil by hydrotreating a narrow cut lube feedstock. The hydrotreating step involves a single hydrotreating zone. U.S. Patent 3,732,154 discloses hydrofinishing the extract or raffinate from a solvent extraction process. The feed to the hydrofinishing step is derived from a highly aromatic source such as a naphthenic distillate. U.S. Patent 4,627,908 relates to a process for improving the bulk oxidation stability and storage stability of lube oil basestocks derived from hydrocracked bright stock. The process involves hydrodenitification of a hydrocracked bright stock followed by hydrofinishing.

U.S. Patent 4,636,299 discloses a process for reducing the pour point of a feedstock containing nitrogen and sulfur-containing compounds wherein the feedstock is solvent extracted with N-methyl-2-pyrrolidone to produce a raffinate, the raffinate is hydrotreated to convert the nitrogen and sulfur containing compounds to ammonia and hydrogen sulfide, stripped of ammonia and hydrogen sulfide and stripped effluent cat dewaxed.

It would be desirable to supplement the conventional solvent refining process so as to produce high VI, low volatility oils which have excellent toxicity, oxidative and thermal stability, fuel economy and cold start properties without incurring any significant yield debit which process requires much lower investment costs than competing technologies such as hydrocracking.

SUMMARY OF THE INVENTION

This invention relates to a process for producing a lubricating oil basestock meeting at least 90% saturates by selectively hydroconverting a raffinate produced from solvent refining a lubricating oil feedstock which comprises:

- (a) conducting the lubricating oil feedstock to a solvent extraction zone and separating therefrom an aromatics rich extract and a paraffins rich raffinate;
- (b) stripping the raffinate of solvent to produce a raffinate feed having a dewaxed oil viscosity index from about 85 to about 105 and a final boiling point of no greater than about 650°C;
- (c) passing the raffinate feed to a first hydroconversion zone and processing the raffinate feed in the presence of a non-acidic hydroconversion catalyst at a

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temperature of from 340 to 420°C, a hydrogen partial pressure of from 1000 to 2500 psig, space velocity of 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 scf/B to produce a first hydroconverted raffinate;

- (d) passing the hydroconverted raffinate from the first hydroconversion zone to a second hydroconversion zone and processing the hydroconverted raffinate in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 400°C provided that the temperature in second hydroconversion is not greater than the temperature in the first hydroconversion zone, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 scf/B to produce a second hydroconverted raffinate;
- (e) passing the second hydroconverted raffinate to a hydrofinishing zone and conducting cold hydrofinishing of the second hydroconverted raffinate in the presence of a hydrofinishing catalyst at a temperature of from 260 to 360°C, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 5 LHSV and a hydrogen to feed ratio of from 500 to 5000 scf/B to produce a hydrofinished raffinate;
- (f) passing the hydrofinished raffinate to a separation zone to remove products having a boiling less than about 250°C; and
- (g) passing the hydrofinished raffinate from step (f) to a dewaxing zone and catalytically dewaxing the hydrofinished raffinate under catalytic dewaxing conditions in the presence of hydrogen and a catalytic dewaxing catalyst comprising a metal hydrogenation component and a crystalline 10 or 12 ring molecular sieve.

In another embodiment, this invention relates to a process for selectively hydroconverting a raffinate produced from solvent refining a lubricating oil feedstock which comprises:

- (a) conducting the lubricating oil feedstock to a solvent extraction zone and separating therefrom an aromatics rich extract and a paraffins rich raffinate;
- (b) stripping the raffinate of solvent to produce a raffinate feed having a dewaxed oil viscosity index from about 85 to about 105 and a final boiling point of no greater than about 650°C;
- (c) passing the raffinate feed to a first hydroconversion zone and processing the raffinate feed in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 420°C, a hydrogen partial pressure of from 1000 to 2500 psig, space velocity of 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 scf/B to produce a first hydroconverted raffinate;
- (d) passing the hydroconverted raffinate from the first hydroconversion zone to a second hydroconversion zone and processing the hydroconverted raffinate in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 400°C provided that the temperature in the second hydroconversion is not greater than the temperature in the first hydroconversion zone, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 scf/B to produce a second hydroconverted raffinate;

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- (e) passing the second hydroconverted raffinate to a hydrofinishing reaction zone and conducting cold hydrofinishing of the second hydroconverted raffinate in the presence of a hydrofinishing catalyst at a temperature of from 260 to 360°C, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 5 LHSV and hydrogen to feed ratio of from 500 to 5000 scf/B to produce a hydrofinished raffinate;
- (f) solvent dewaxing the hydrofinished raffinate under solvent dewaxing conditions to obtain a dewaxed oil having a pour point less than about 10°C; and
- (g) catalytically dewaxing the solvent dewaxed oil under catalytic dewaxing conditions in the presence of hydrogen and a catalytic dewaxing catalyst comprising a metal hydrogenation component and a crystalline 10 or 12 ring molecular sieve to produce a dewaxed basestock.

In yet another embodiment, the cold hydrofinishing step is moved from after the second hydroconversion zone to after the catalytic dewaxing step for either of the embodiments set forth above.

The process according to the invention produces in good yields a basestock which has VI and volatility properties meeting future industry engine oil standards while achieving good oxidation stability, cold start, fuel economy, and thermal stability properties. In addition, toxicity tests show that the basestock has excellent toxicological properties as measured by tests such as the FDA(c) test.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of NOACK volatility vs. viscosity for a 100N basestock.

Figure 2 is a schematic flow diagram of the hydroconversion process.

Figure 3 is a graph showing VI HOP vs. conversion at different pressures.

Figure 4 is a graph showing temperature in the first hydroconversion zone as a function of days on oil at a fixed pressure.

Figure 5 is a graph showing saturates concentration as a function of reactor temperature for a fixed VI product.

Figure 6 is a graph showing toxicity as a function of temperature and pressure in the cold hydrofinishing step.

Figure 7 is a graph showing control of saturates concentration by varying conditions in the cold hydrofinishing step.

Figure 8 is a graph showing the correlation between the DMSO screener test and the FDA (c) test.

Figure 9 is a graph showing the catalytic dewaxing of dewaxed oil and total liquid products.

Figure 10 is a graph showing the comparison catalytic dewaxing a total liquid product vs. solvent dewaxing to the same pour point.

DETAILED DESCRIPTION OF THE INVENTION

The solvent refining of select crude oils to produce lubricating oil basestocks typically involves atmospheric distillation, vacuum distillation, extrac-

tion, dewaxing and hydrofinishing. Because basestocks having a high isoparaffin content are characterized by having good viscosity index (VI) properties and suitable low temperature properties, the crude oils used in the solvent refining process are typically paraffinic crudes. One method of classifying lubricating oil basestocks is that used by the American Petroleum Institute (API). API Group II basestocks have a saturates content of 90 wt% or greater, a sulfur content of not more than 0.03 wt% and a viscosity index (VI) greater than 80 but less than 120. API Group III basestocks are the same as Group II basestocks except that the VI is greater than or equal to 120.

Generally, the high boiling petroleum fractions from atmospheric distillation are sent to a vacuum distillation unit, and the distillation fractions from this unit are solvent extracted. The residue from vacuum distillation which may be deasphalted is sent to other processing. Other feeds to solvent extraction include waxy streams such as dewaxed oils and foots oils.

The solvent extraction process selectively dissolves the aromatic components in an extract phase while leaving the more paraffinic components in a raffinate phase. Naphthenes are distributed between the extract and raffinate phases. Typical solvents for solvent extraction include phenol, furfural and N-methyl pyrrolidone. By controlling the solvent to oil ratio, extraction temperature and method of contacting distillate to be extracted with solvent, one can control the degree of separation between the extract and raffinate phases.

In recent years, solvent extraction has been replaced by hydrocracking as a means for producing high VI basestocks in some refineries. The hydrocracking process utilizes low quality feeds such as feed distillate from the vacuum distillation unit or other refinery streams such as vacuum gas oils and coker gas oils. The

catalysts used in hydrocracking are typically sulfides of Ni, Mo, Co and W on an acidic support such as silica/alumina or alumina containing an acidic promoter such as fluorine. Some hydrocracking catalysts also contain highly acidic zeolites. The hydrocracking process may involve hetero-atom removal, aromatic ring saturation, dealkylation of aromatics rings, ring opening, straight chain and side-chain cracking, and wax isomerization depending on operating conditions. In view of these reactions, separation of the aromatics rich phase that occurs in solvent extraction is an unnecessary step since hydrocracking reduces aromatics content to very low levels.

By way of contrast, the process of the present invention utilizes a three step hydroconversion of the raffinate from the solvent extraction unit under conditions which minimizes hydrocracking and passing waxy components through the process without wax isomerization. Thus, dewaxed oil (DWO) and low value foots oil streams can be added to the raffinate feed whereby the wax molecules pass unconverted through the process and may be recovered as a valuable by-product. Moreover, unlike hydrocracking, the present process takes place without disengagement, i.e., without any intervening steps involving gas/liquid products separations. The product of the subject three step process has a saturates content greater than 90 wt%, preferably greater than 95 wt%. Thus product quality is similar to that obtained from hydrocracking without the high temperatures and pressures required by hydrocracking which results in a much greater investment expense.

The raffinate from the solvent extraction is preferably under-extracted, i.e., the extraction is carried out under conditions such that the raffinate yield is maximized while still removing most of the lowest quality molecules from the feed. Raffinate yield may be maximized by controlling extraction conditions, for example, by lowering the solvent to oil treat ratio and/or decreasing the extraction temperature. The raffinate from the solvent extraction unit is stripped of solvent and then sent to a

first hydroconversion unit containing a hydroconversion catalyst. This raffinate feed has a viscosity index of from about 85 to about 105 and a boiling range not to exceed about 650°C, preferably less than 600° C, as determined by ASTM 2887 and a viscosity of from 3 to 15 cSt at 100°C.

Hydroconversion catalysts are those containing Group VIB metals (based on the Periodic Table published by Fisher Scientific), and non-noble Group VIII metals, i.e., iron, cobalt and nickel and mixtures thereof. These metals or mixtures of metals are typically present as oxides or sulfides on refractory metal oxide supports.

It is important that the metal oxide support be non-acidic so as to control cracking. A useful scale of acidity for catalysts is based on the isomerization of 2-methyl-2-pentene as described by Kramer and McVicker, J. Catalysis, 92, 355 (1985). In this scale of acidity, 2-methyl-2-pentene is subjected to the catalyst to be evaluated at a fixed temperature, typically 200°C. In the presence of catalyst sites, 2-methyl-2-pentene forms a carbenium ion. The isomerization pathway of the carbenium ion is indicative of the acidity of active sites in the catalyst. Thus weakly acidic sites form 4-methyl-2-pentene whereas strongly acidic sites result in a skeletal rearrangement to 3-methyl-2-pentene with very strongly acid sites forming 2,3-dimethyl-2-butene. The mole ratio of 3-methyl-2-pentene to 4-methyl-2-pentene can be correlated to a scale of acidity. This acidity scale ranges from 0.0 to 4.0. Very weakly acidic sites will have values near 0.0 whereas very strongly acidic sites will have values approaching 4.0. The catalysts useful in the present process have acidity values of less than about 0.5, preferably less than about 0.3. The acidity of metal oxide supports can be controlled by adding promoters and/or dopants, or by controlling the nature of the metal oxide support, e.g., by controlling the amount of silica incorporated into a silica-alumina support. Examples of promoters and/or

dopants include halogen, especially fluorine, phosphorus, boron, yttria, rare-earth oxides and magnesia. Promoters such as halogens generally increase the acidity of metal oxide supports while mildly basic dopants such as yttria or magnesia tend to decrease the acidity of such supports.

Suitable metal oxide supports include low acidic oxides such as silica, alumina or titania, preferably alumina. Preferred aluminas are porous aluminas such as gamma or eta having average pore sizes from 50 to 200Å, preferably 75 to 150Å, a surface area from 100 to 300 m²/g, preferably 150 to 250 m²/g and a pore volume of from 0.25 to 1.0 cm³/g, preferably 0.35 to 0.8 cm³/g. The supports are preferably not promoted with a halogen such as fluorine as this generally increases the acidity of the support above 0.5.

Preferred metal catalysts include cobalt/molybdenum (1-5% Co as oxide, 10-25% Mo as oxide) nickel/molybdenum (1-5% Ni as oxide, 10-25% Co as oxide) or nickel/tungsten (1-5% Ni as oxide, 10-30% W as oxide) on alumina. Especially preferred are nickel/molybdenum catalysts such as KF-840.

Hydroconversion conditions in the first hydroconversion unit include a temperature of from 340 to 420°C, preferably 350 to 400°C, a hydrogen partial pressure of from 1000 to 2500 psig (7.0 to 17.3 mPa), preferably 1000 to 2000 psig (7.0 to 13.9 mPa), a space velocity of from 0.2 to 3.0 LHSV, preferably 0.3 to 1.0 LHSV, and a hydrogen to feed ratio of from 500 to 5000 Scf/B (89 to 890 m³/m³), preferably 2000 to 4000 scf/B (356 to 712 m³/m³).

The hydroconverted raffinate from the first hydroconversion unit is conducted to a second hydroconversion unit. The hydroconverted raffinate is preferably passed through a heat exchanger located between the first and second

hydroconversion units so that the second hydroconversion unit can be run at cooler temperatures, if desired. Temperatures in the second hydroconversion unit should not exceed the temperature used in the first hydroconversion unit. Conditions in the second hydroconversion unit include a temperature of from 340 to 400°C, preferably 350 to 385°C, a hydrogen partial pressure of from 1000 to 2500 psig (7.0 to 17.3 Mpa), preferably 1000 to 2000 psig (7.0 to 13.9 Mpa), a space velocity of from 0.2 to 3.0 LHSV, preferably 0.3 to 1.5 LHSV, and a hydrogen to feed ratio of from 500 to 5000 Scf/B (89 to 890 m³/m³), preferably 2000 to 4000 Scf/B (356 to 712 m³/m³). The catalyst in the second hydroconversion unit can be the same as in the first hydroconversion unit, although a different hydroconversion catalyst may be used.

The hydroconverted raffinate from the second hydroconversion unit is then conducted to cold hydrofinishing unit. A heat exchanger is preferably located between these units. Reaction conditions in the hydrofinishing unit are mild and include a temperature of from 260 to 360°C, preferably 290 to 350°C, more preferably 290 to 330°C, a hydrogen partial pressure of from 1000 to 2500 psig (7.0 to 17.3 mPa), preferably 1000 to 2000 psig (7.0 to 13.9 mPa), a space velocity of from 0.2 to 5.0 LHSV, preferably 0.7 to 3.0 LHSV, and a hydrogen to feed ratio of from 500 to 5000 scf/B (89 to 890 m³/m³), preferably 2000 to 4000 scf/B (356 to 712 m³/m³). The catalyst in the cold hydrofinishing unit may be the same as in the first hydroconversion unit. However, more acidic catalyst supports such as silica-alumina, zirconia and the like may be used in the cold hydrofinishing unit.

In order to prepare a finished basestock, the hydroconverted raffinate from the hydrofinishing unit is conducted to a separator, e.g., a vacuum stripper (or fractionation) to separate out low boiling products if the separator is followed by a catalytic dewaxing step. Such products may include hydrogen sulfide and ammonia formed in the first two reactors. If desired, a stripper may be situated between the

second hydroconversion unit and the hydrofinishing unit, but this is not essential to produce basestocks according to the invention.

The hydroconverted raffinate separated from the separator is then conducted to a dewaxing unit. Catalytic dewaxing, solvent dewaxing or a combination may accomplish dewaxing thereof.

The catalysts useful in the catalytic dewaxing step include crystalline 10 and 12 ring molecular sieves and a metal hydrogenation component. Crystalline molecular sieves include aluminosilicates and aluminum phosphates. Examples of crystalline aluminosilicates include zeolites such as ZSM-5, ZSM-11, ZSM-12, theta-1 (ZSM-22), ZSM-23, ZSM-35, ferrierite, ZSM-38, ZSM-48, ZSM-57, beta, mordenite and offretite. Examples of crystalline aluminum phosphates include SAPO-11, SAPO-41, SAPO-31, MAPO-11 and MAPO-31. Preferred molecular sieves include ZSM-5, theta-1, ZSM-23, ferrierite and SAPO-11.

The dewaxing catalyst may also contain an amorphous component. The acidity of the amorphous component is preferably from 0.3 to 2.5, preferably 0.5 to 2.0 on the Kramer/McVicker acidity scale described above. Examples of amorphous materials include silica-alumina, halogenated alumina, acidic clays, silica-magnesia, yttria silica-alumina and the like. Especially preferred is silica-alumina.

If the dewaxing catalyst contains an amorphous component, the crystalline molecular sieve/metal hydrogenation component/amorphous component may be composited together. The hydrogenation metal can be deposited on each component separately or can be deposited on the composited catalyst. In the alternative, the crystalline molecular sieve and amorphous component can be in a

layered configuration. Preferably, the top layer in the reaction vessel is the amorphous component and the lower layer is the crystalline molecular sieve, although the configuration can be reversed with the top layer as the molecular sieve and the bottom layer as the amorphous component. In the layered configuration, the hydrogenation metal should be deposited on both the molecular sieve and the amorphous component.

The metal hydrogenation component of the dewaxing catalyst may be at least one metal from the Group VIB and Group VIII of the Periodic Table (published by Sargent-Welch Scientific Company). Preferred metals are Group VIII noble metals, especially palladium and platinum.

The dewaxing catalyst may contain, based on the weight of total catalyst, from 5 to 95 wt% of crystalline molecular sieve, from 0 to 90 wt% of amorphous component and from 0.1 to 30 wt% of metal hydrogenation component with the balance being matrix material.

The dewaxing catalyst may also include a matrix or binder which is a material resistant to process conditions and which is substantially non-catalytic under reaction conditions. Matrix materials may be synthetic or naturally occurring materials such as clays, silica and metal oxides. Matrix materials which are metal oxides include single oxides such as alumina, binary compositions such as silica-magnesia and ternary compositions such as silica-alumina-zirconia.

Process conditions in the catalytic dewaxing zone include a temperature of from 240 to 420°C, preferably 270 to 400°C, a hydrogen partial pressure of from 3.45 to 34.5 mPa (500 to 5000 psi), preferably 5.52 to 20.7 mPa, a liquid hourly space velocity of from 0.1 to 10 v/v/hr, preferably 0.5 to 3.0, and a hydrogen

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circulation rate of from 89 to 1780 m³/m³ (500 to 10000 scf/B), preferably 178 to 890 m³/m³.

In an alternative embodiment, the hydroconverted raffinate from the cold hydrofinishing unit or the hydroconverted raffinate from the hydroconversion zone may be conducted to a solvent dewaxer with or without, preferably with a stripping step to remove low boiling products. The solvent dewaxing process typically involves mixing feed with solvent at atmospheric pressure, separating precipitated wax and recovering solvent for recycling. The hydroconverted raffinate is mixed with chilled solvent to form an oil-solvent solution and precipitated wax is thereafter separated by, for example filtration. The temperature and solvent are selected so that the oil is dissolved by the chilled solvent while the wax is precipitated. The solvent dewaxer may then be followed by a catalytic dewaxing step such as described above. Because solvent dewaxing typically occurs at atmospheric pressure, it may be necessary to pressurize the solvent dewaxed oil prior to the catalytic dewaxing step.

A particularly suitable solvent dewaxing process involves the use of a cooling tower where solvent is prechilled and added incrementally at several points along the height of the cooling tower. The oil-solvent mixture is agitated during the chilling step to permit substantially instantaneous mixing of the prechilled solvent with the oil. The prechilled solvent is added incrementally along the length of the cooling tower so as to maintain an average chilling rate at or below 10°F/minute, usually between about 1 to about 0°F/minute. The final temperature of the oil-solvent/precipitated wax mixture in the cooling tower will usually be between 0 and 50°F (-17.8 to 10°C). The mixture may then be sent to a scraped surface chiller to separate precipitated wax from the mixture.

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In general, the amount of solvent added will be sufficient to provide a liquid/solid weight ration between the range of 5/1 and 20/1 at the dewaxing temperature and a solvent/oil volume ratio between 1.5/1 to 5/1. The solvent dewaxed oil is typically dewaxed to a pour point from +10°C to -20°C.

Representative dewaxing solvents are aliphatic ketones having 3-6 carbon atoms such as methyl ethyl ketone and methyl isobutyl ketone, low molecular weight hydrocarbons such as propane and butane, and mixtures thereof. The solvents may be mixed with other solvents such as benzene, toluene or xylene. Further descriptions of solvent dewaxing process useful herein are disclosed in U.S. Patents 3,773,650 and 3,775,288 which are incorporated herein in their entirety.

The solvent dewaxed oil may be suitable as a lubricating oil base-stock. However in the present embodiment, the solvent dewaxed oil is subjected to a catalytic dewaxing step to further lower the pour point using the catalytic dewaxing catalysts described above. The sequence of solvent dewaxing followed by catalytic dewaxing is designated as trim dewaxing. As noted previously, the dewaxing catalyst may comprise a molecular sieve loaded with a metal hydrogenation component, may be a composite of a metal loaded combination of crystalline molecular sieve and amorphous component or may be a layered configuration wherein the layers contain an amorphous component, a crystalline molecular sieve, and a metal hydrogenation component.

In either processing sequence, i.e., 2-step hydroconversion - cold hydrofinishing - catalytic dewaxing, or 2-step hydroconversion - cold hydrofinishing - solvent dewaxing - catalytic dewaxing, the final catalytic dewaxing step may be followed by a second cold hydrofinishing step under the cold hydrofinishing conditions described above. This second cold hydrofinishing step would be used in those

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instances where needed to meet product quality requirements such as color or light stability.

Alternatively, the processing sequences may omit the first cold hydrofinishing step and use only a final cold hydrofinishing step. These sequences are defined as 2-step hydroconversion - catalytic dewaxing - cold hydrofinishing, or hydroconversion - solvent dewaxing - catalytic dewaxing - cold hydrofinishing.

The lubricating oil basestock produced by the process according to the invention is characterized by the following properties: viscosity index of at least about 100, preferably at least 105 and saturates of at least 90%, preferably at least 95 wt%, NOACK volatility improvement (as measured by DIN 51581) over raffinate feedstock of at least about 3 wt%, preferably at least about 5 wt%, at the same viscosity within the range 3.5 to 6.5 cSt viscosity at 100°C, pour point of -15°C or lower, and a low toxicity as determined by IP346 or phase 1 of FDA (c). IP346 is a measure of polycyclic aromatic compounds. Many of these compounds are carcinogens or suspected carcinogens, especially those with so-called bay regions [see Accounts Chem. Res. 17, 332(1984) for further details]. The present process reduces these polycyclic aromatic compounds to such levels as to pass carcinogenicity tests. The FDA (c) test is set forth in 21 CFR 178.3620 and is based on ultraviolet absorbances in the 300 to 359 nm range.

As can be seen from Figure 1, NOACK volatility is related to VI for any given basestock. The relationship shown in Figure 1 is for a light basestock (about 100N). If the goal is to meet a 22 wt% NOACK volatility for a 100N oil, then the oil should have a VI of about 110 for a product with typical-cut width, e.g., 5 to 50% off by GCD at 60°C. Volatility improvements can be achieved with lower VI product by decreasing the cut width. In the limit set by zero cut width, one can

meet 22% NOACK volatility at a VI of about 100. However, this approach, using distillation alone, incurs significant yield debits.

Hydrocracking is also capable of producing high VI, and consequently low NOACK volatility basestocks, but is less selective (lower yields) than the process of the invention. Furthermore both hydrocracking and processes such as wax isomerization destroy most of the molecular species responsible for the solvency properties of solvent refined oils. The latter also uses wax as a feedstock whereas the present process is designed to preserve wax as a product and does little, if any, wax conversion.

The process of the invention is further illustrated by Figure 2. The feed 8 to vacuum pipestill 10 is typically an atmospheric reduced crude from an atmospheric pipestill (not shown). Various distillate cuts shown as 12 (light), 14 (medium) and 16 (heavy) may be sent to solvent extraction unit 30 via line 18. These distillate cuts may range from about 200°C to about 650°C. The bottoms from vacuum pipestill 10 may be sent through line 22 to a coker, a visbreaker or a deasphalting extraction unit 20 where the bottoms are contacted with a deasphalting solvent such as propane, butane or pentane. The deasphalted oil may be combined with distillate from the vacuum pipestill 10 through line 26 provided that the deasphalted oil has a boiling point no greater than about 650°C or is preferably sent on for further processing through line 24. The bottoms from deasphalter 20 can be sent to a visbreaker or used for asphalt production. Other refinery streams may also be added to the feed to the extraction unit through line 28 provided they meet the feedstock criteria described previously for raffinate feedstock.

In extraction unit 30, the distillate cuts are solvent extracted with N-methyl pyrrolidone and the extraction unit is preferably operated in countercurrent

mode. The solvent-to-oil ratio, extraction temperature and percent water in the solvent are used to control the degree of extraction, i.e., separation into a paraffins rich raffinate and an aromatics rich extract. The present process permits the extraction unit to operate to an "under extraction" mode, i.e., a greater amount of aromatics in the paraffins rich raffinate phase. The aromatics rich extract phase is sent for further processing through line 32. The raffinate phase is conducted through line 34 to solvent stripping unit 36. Stripped solvent is sent through line 38 for recycling and stripped raffinate is conducted through line 40 to first hydroconversion unit 42.

The first hydroconversion unit 42 contains KF-840 catalyst which is nickel/molybdenum on an alumina support and available from Akzo Nobel. Hydrogen is admitted to unit or reactor 42 through line 44. Gas chromatographic comparisons of the hydroconverted raffinate indicate that almost no wax isomerization is taking place. While not wishing to be bound to any particular theory since the precise mechanism for the VI increase which occurs in this stage is not known with certainty, it is known that heteroatoms are being removed, aromatic rings are being saturated and naphthene rings, particularly multi-ring naphthenes, are selectively eliminated.

Hydroconverted raffinate from hydroconversion unit 42 is conducted through line 46 to heat exchanger 48 where the hydroconverted raffinate stream may be cooled if desired. The cooled raffinate stream is conducted through line 50 to a second hydroconversion unit 52. Additional hydrogen, if needed, is added through line 54. This second hydroconversion unit is operated at a lower temperature (when required to adjust product quality) than the first hydroconversion unit 42. While not wishing to bound to any theory, it is believed that the capability to operate the second unit 52 at lower temperature shifts the equilibrium conversion between saturated species and other unsaturated hydrocarbon species back towards increased

saturates concentration. In this way, the concentration of saturates can be maintained at greater than 90 wt% by appropriately controlling the combination of temperature and space velocity in second hydroconversion unit 52.

Hydroconverted raffinate from unit 52 is conducted through line 54 to a second heater exchanger 56. After additional heat is removed through heat exchanger 56, cooled hydroconverted raffinate is conducted through line 58 to cold hydrofinishing unit 60. Temperatures in the hydrofinishing unit 60 are more mild than those of hydroconversion units 42 and 52. Temperature and space velocity in cold hydrofinishing unit 60 are controlled to reduce the toxicity to low levels, i.e., to a level sufficiently low to pass standard toxicity tests. This may be accomplished by reducing the concentration of polynuclear aromatics to very low levels.

Hydrofinished raffinate is then conducted through line 64 to separator 68. Light liquid products and gases are separated and removed through line 72. The remaining hydrofinished raffinate is conducted through line 70 to dewaxing unit 74. Dewaxing may occur by the use of solvents introduced through line 78 which may be followed by cooling, by catalytic dewaxing or by a combination thereof. If dewaxing unit 74 utilizes solvent dewaxing, then hydrofinished raffinate may be conducted directly from reactor 60 to dewaxing unit 74 without going through separator 68. The solvent dewaxed oil from unit 74 may then be sent to a second dewaxing unit (not shown) wherein catalytic dewaxing of the solvent dewaxed oil occurs. If dewaxing unit 74 utilizes catalytic dewaxing, then the hydrofinished raffinate from reactor 60 should go through separator 68 before being conducted to dewaxing unit 74. Catalytic dewaxing involves selective hydrocracking with or without hydroisomerization as a means to create low pour point lubricant basestocks. Solvent dewaxing with optional cooling separates waxy molecules from the hydroconverted lubricant basestock thereby lowering the pour point. In markets where

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waxes are valued, hydrofinished raffinate is preferably contacted with methyl isobutyl ketone followed by the DILCHILL® Dewaxing Process developed by Exxon. This method is well known in the art. Finished lubricant basestock is removed through line 76 and waxy product through line 80.

While not wishing to be bound by any theory, the factors affecting saturates, VI and toxicity are discussed as follows. The term "saturates" refers to the sum of all saturated rings, paraffins and isoparaffins. In the present raffinate hydroconversion process, under-extracted (e.g. 92 VI) light and medium raffinates including isoparaffins, n-paraffins, naphthenes and aromatics having from 1 to about 6 rings are processed over a non-acidic catalyst which primarily operates to (a) hydrogenate aromatic rings to naphthenes and (b) convert ring compounds to leave isoparaffins in the lubes boiling range by either dealkylation or by ring opening of naphthenes. The catalyst is not an isomerization catalyst and therefore leaves paraffinic species in the feed largely unaffected. High melting paraffins and isoparaffins are removed by a subsequent dewaxing step. Thus other than residual wax the saturates content of a dewaxed oil product is a function of the irreversible conversion of rings to isoparaffins and the reversible formation of naphthenes from aromatic species.

To achieve a basestock viscosity index target, e.g., 110 VI, for a fixed catalyst charge and feed rates, hydroconversion reactor temperature is the primary driver. Temperature sets the conversion (arbitrarily measured here as the conversion to 370°C-) which is nearly linearly related to the VI increase, irrespective of pressure. This is shown in Figure 3 relating the VI increase (VI HOP) to conversion. For a fixed pressure, the saturates content of the product depends on the conversion, i.e., the VI achieved, and the temperature required to achieve conversion. At start of run on a typical feed, the temperature required to achieve the target VI may be only

350°C and the corresponding saturates of the dewaxed oil will normally be in excess of 90 wt%, for processes operating at or above 1000 psig (7.0 mPa) H₂. However, the catalyst deactivates with time such that the temperature required to achieve the same conversion (and the same VI) must be increased. Over a 2 year period, the temperature may increase by 25 to 50°C depending on the catalyst, feed and the operating pressure. A typical deactivation profile is illustrated in Figure 4 which shows temperature as a function of days on oil at a fixed pressure. In most circumstances, with process rates of about 1.0 v/v/hr or less and temperatures in excess of 350°C, the saturates associated with the ring species left in the product are determined only by the reactor temperature, i.e., the naphthene population reaches the equilibrium value for that temperature.

Thus as the reactor temperature increases from about 350°C, saturates will decline along a smooth curve defining a product of fixed VI. Figure 5 shows three typical curves for a fixed product of 112 VI derived from a 92 VI feed by operating at a fixed conversion. Saturates are higher for a higher pressure process in accord with simple equilibrium considerations. Each curve shows saturates falling steadily with temperatures increasing above 350°C. At 600 psig (4.24 mPa) H₂, the process is incapable of simultaneously meeting the VI target and the required saturates (90+ wt%). The projected temperature needed to achieve 90+ wt% saturates at 600 psig (4.24 mPa) is well below that which can be reasonably achieved with the preferred catalyst for this process at any reasonable feed rate/catalyst charge. However, at 1000 psig H₂ and above, the catalyst can simultaneously achieve 90 wt% saturates and the target VI.

An important aspect of the invention is that a temperature staging strategy can be applied to maintain saturates at 90+ wt% for process pressures of 1000 psig (7.0 mPa) H₂ or above without disengagement of sour gas and without the

use of a polar sensitive hydrogenation catalyst such as massive nickel that is employed in typical hydrocracking schemes. The present process also avoids the higher temperatures and pressures of the conventional hydrocracking process. This is accomplished by separating the functions to achieve VI, saturates and toxicity using a cascading temperature profile over 3 reactors without the expensive insertion of stripping, recompression and hydrogenation steps. API Group II and III basestocks (API Publication 1509) can be produced in a single stage, temperature controlled process.

Toxicity of the basestock is adjusted in the cold hydrofinishing step. For a given target VI, the toxicity may be adjusted by controlling the temperature and pressure. This is illustrated in Figure 6 which shows that higher pressures allows a greater temperature range to correct toxicity.

The invention is further illustrated by the following non-limiting examples.

EXAMPLE 1

This example summarizes functions of each reactor A, B and C. Reactors A and B affect VI though A is controlling. Each reactor can contribute to saturates, but Reactors B and C may be used to control saturates. Toxicity is controlled primarily by reactor C.

TABLE 1

<u>Product Parameter</u>	<u>Reactor A</u>	<u>Reactor B</u>	<u>Reactor C</u>
VI	X	X	
Saturates		X	X
Toxicity			X

EXAMPLE 2

This example illustrates the product quality of oils obtained from the process according to the invention. Reaction conditions and product quality data for start of run (SOR) and end of run (EOR) are summarized in Tables 2 and 3.

As can be seen from the data in Table 2 for the 250N feed stock, reactors A and B operate at conditions sufficient to achieve the desired viscosity index, then, with adjustment of the temperature of reactor C, it is possible to keep saturates above 90 wt% for the entire run length without compromising toxicity (as indicated by DMSO screener result; see Example 6). A combination of higher temperature and lower space velocity in reactor C (even at end of run conditions in reactors A and B) produced even higher saturates, 96.2%. For a 100N feed stock, end-of-run product with greater than 90% saturates may be obtained with reactor C operating as low as 290C at 2.5 v/v/h (Table 3).

TABLE 2

Reactor	---SOR---		---EOR---		---EOR---	
	Temp. (°C)	LHSV (v/v/hr)	Temp. (°C)	LHSF (v/v/hr)	Temp. (°C)	LHSV (v/v/hr)
A	352	0.7	400	0.7	400	0.7
B	352	1.2	400	1.2	400	1.2
C	290	2.5	290	2.5	350	2.5
					350	1.0

* Other Conditions: 1800 psig (12.5 mPa) H₂ inlet pressure, 2400 scf/B (427 m³/m³)

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Dewaxed Oil Properties	250N(1) Feed	SOR	EOR	EOR	EOR
100°C Viscosity, cSt	7.34	5.81	5.53	5.47	5.62
40°C Viscosity, cSt	54.41	34.28	31.26	30.63	32.08
Viscosity Index	93	111	115	115	114
Pour Point, °C	-18	-18	-16	-18	-19
Saturates, wt%	58.3	100	85.2	91	96.2
DMSO Screener for toxicity(2)	0.30	0.02	0.06	0.10	0.04
370°C Yield, wt. on raffinate feed	100	87	81	81	82

(1) 93 VI under extracted feed.

(2) Maximum ultra-violet absorbance at 340 to 350 nm.

TABLE 3

<u>Reactor</u>	<u>SOR</u>		<u>EOR</u>	
	<u>Temp.</u> <u>(°C)</u>	<u>LHSV</u> <u>(v/v/hr)</u>	<u>Temp.</u> <u>(°C)</u>	<u>LHSV</u> <u>(v/v/hr)</u>
A	355	0.7	394	0.7
B	355	1.2	394	1.2
C	290	2.5	290	2.5

* Other Conditions: 1800 psig (12.5 mPa) H₂ inlet pressure, 2400 scf/B (427 m³/m³).

<u>Dewaxed Oil Properties</u>	<u>100N (1)</u> <u>Feed</u>	<u>SOR</u>	<u>EOR</u>
100°C Viscosity, cSt	4.35	3.91	3.83
40°C Viscosity, cSt	22.86	18.23	17.36
Viscosity Index	95	108	112
Pour Point, °C	-18	-18	-18
Saturates, wt%	64.6	99	93.3
DMSO Screener for toxicity (2)	0.25	0.01	0.03
370°C+ Yield, wt% on raffinate feed	93	80	75

- (1) 95 VI under extracted feed.
 (2) Maximum ultra-violet absorbance at 340 to 350 nm.

EXAMPLE 3

The effect of temperature and pressure on the concentration of saturates (dewaxed oil) at constant VI is shown in this example for processing the under extracted 250N raffinate feed. Dewaxed product saturates equilibrium plots (Figure 5) were obtained at 600, 1200 and 1800 psig (4.24, 8.38 and 12.5 mPa) H₂ pressure. Process conditions were 0.7 LHSV (reactor A + B) and 1200 to 2400 SCF/B (214 to 427 m³/m³). Both reactors A and B were operating at the same temperature (in the range 350 to 415°C).

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As can be seen from the figure it is not possible to achieve 90 wt% saturates at 600 psig (4.14 mPa) hydrogen partial pressure. While in theory, one could reduce the temperature to reach the 90 wt% target, the space velocity would be impractically low. The minimum pressure to achieve the 90 wt% at reasonable space velocities is about 1000 psig (7.0 mPa). Increasing the pressure increases the temperature range which may be used in the first two reactors (reactor A and B). A practical upper limit to pressure is set by higher cost metallurgy typically used for hydrocrackers, which the process of the invention can avoid.

EXAMPLE 4

The catalyst deactivation profile as reflected by temperature required to maintain product quality is shown in this example. Figure 4 is a typical plot of isothermal temperature (for reactor A, no reactor B) required to maintain a VI increase of 18 points versus time on stream. KF840 catalyst was used for reactors A and C. Over a two year period, reactor A temperatures could increase by about 50°C. This will affect the product saturates content. Strategies to offset a decline in product saturates as reactor A temperature is increased are shown below.

EXAMPLE 5

This example demonstrates the effect of temperature staging between the first (reactor A) and second (reactor B) hydroconversion units to achieve the desired saturates content for a 1400 psig (9.75 mPa) H₂ process with a 93 VI raffinate feed.

TABLE 4

Reactor Sequence:	Base Case		Temperature Staged Case		
	<u>Reactor</u>	T (°C)	LHSV (v/v/h)	T (°C)	LHSV (v/v/h)
	A	390	0.7	390	0.7
	B	390	1.2	350	0.5
	C	290	2.5	290	2.5
Dewaxed Oil Viscosity Index		114		115	
Dewaxed Oil Saturates, wt%		80		96	

A comparison of the base case versus the temperature staged case demonstrates the merit of operating reactor B at lower temperature and space velocities. The bulk saturates content of the product was restored to the thermodynamic equilibrium at the temperature of reactor B.

EXAMPLE 6

The effects of temperature and pressure in the cold hydrofinishing unit (reactor C) on toxicity are shown in this example. The toxicity is estimated using a dimethyl sulphoxide (DMSO) based screener test developed as a surrogate for the FDA (c) test. The screener and the FDA (c) test are both based on the ultra-violet spectrum of a DMSO extract. The maximum absorbance at 345+/-5 nm in the screener test was shown to correlate well with the maximum absorbance between 300-359 nm in the FDA (c) test as shown in Figure 8. The upper limit of acceptable toxicity using the screener test is 0.16 absorbance units. As shown in Figure 6, operating at 1800 psig (12.7 Mpa) versus 1200 psig (8.38 Mpa) hydrogen partial pressure allows the use of a much broader temperature range (e.g., 290 to ~360°C versus a maximum of only about 315°C when operating at 1200 psig H₂ (8.35 Mpa)) in the cold hydrofinisher to achieve a non-toxic product. The next example

demonstrates that higher saturates, non-toxic products can be made when reactor C is operated at higher temperature.

EXAMPLE 7

This example is directed to the use of the cold hydrofinishing (reactor C) unit to optimize saturates content of the oil product. Reactors A and B were operated at 1800 psig (12.7 mPa) hydrogen partial pressure, 2400 scf/B (427 m³/m³) treat gas rate, 0.7 and 1.2 LHSV respectively and at a near end-of-run (EOR) temperature of 400°C on a 92 VI 250N raffinate feed. The effluent from reactors A and B contains just 85% saturates. Table 5 shows the conditions used in reactor C needed to render a product that is both higher saturates content and is non-toxic. At 350°C, reactor C can achieve 90+% saturates even at space velocities of 2.5 v/v/hr. At lower LHSV, saturates in excess of 95% are achieved.

TABLE 5

Run Number	RUNS			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Temperature, °C	290	330	350	350
LHSV, v/v/hr	2.5	2.5	2.5	1.0
H ₂ Pressure, psig	1800	1800	1800	1800
Treat Gas Rate, SCF/B	2400	2400	2400	2400
DWO VI	115	114	115	114
DWO Saturates, wt%	85	88	91	96
DMSO Screener for Toxicity(1)	0.06	0.05	0.10	0.04

(1) Maximum ultra-violet absorbance at 340-350 nm

Figure 7 further illustrates the flexible use of reactor C. As shown in Figure 7, optimization of reactor C by controlling temperature and space velocity gives Group II basestocks.

EXAMPLE 8

This example demonstrates that feeds in addition to raffinates and dewaxed oils can be upgraded to higher quality basestocks. The upgrading of low value foots oil streams is shown in this example. Foots oil is a waxy by-product stream from the production of low oil content finished wax. This material can be used either directly or as a feed blendstock with under extracted raffinates or dewaxed oils. In the example below (Table 6), foots oil feeds were upgraded at 650 psig (4.58 mPa) H₂ to demonstrate their value in the context of this invention. Reactor C was not included in the processing. Two grades of foots oil, a 500N and 150N, were used as feeds.

TABLE 6

	500 N		150 N	
	Feed	Product	Feed	Product
Temperature, °C (Reactor A/B)	-	354	-	354
Treat Gas rate (TGR), Scf/B, (m ³ /m ³)	-	500 (89)	-	500 (89)
Hydrogen partial pressure, psig (mPa)	-	650 (4.58)	-	650 (4.58)
LHSV, v/v/hr (Reactor A+B)	-	1.0	-	1.0
wt% 370°C - on feed	0.22	3.12	1.10	2.00
<u>370°C+ DWO Inspections</u>				
40°C viscosity, cSt	71.01	48.80	25.01	17.57
100°C viscosity, cSt	8.85	7.27	4.77	4.01
VI/Pour Point, °C	97/-15	109/-17 ⁽²⁾	111/-8	129/-9 ⁽²⁾
Saturates, wt%	73.4	82.8 ⁽¹⁾	79.03	88.57 ⁽¹⁾
GCD NOACK, wt%	4.2	8.0	19.8	23.3
Dry Wax, wt%	66.7	67.9	83.6	83.3
DWO Yield, wt% of Foots Oil Feed	33.2	31.1	16.2	15.9

⁽¹⁾ Saturates improvement will be higher at higher hydrogen pressures

⁽²⁾ Excellent blend stock

Table 6 shows that both a desirable basestock with significantly higher VI and saturates content and a valuable wax product can be recovered from foots oil. In general, since wax molecules are neither consumed or formed in this process, inclusion of foots oil streams as feed blends provides a means to recover the valuable wax while improving the quality of the resultant base oil product.

EXAMPLE 9

This example illustrates the advantage of catalytic trim dewaxing a solvent dewaxed hydrotreated raffinate. The trim catalytic dewaxed products, even though they have lower VI, have much better low temperature properties (products as defined by lower Brookfield Viscosity) than the corresponding solvent dewaxed feed. Trim dewaxing refers to the process of solvent dewaxing followed by catalytic dewaxing.

A raffinate product made under the conditions in Table 7 was topped at 370°C to give a 370°C+ product which was solvent dewaxed using MIBK in a 3:1 solvent to raffinate product ratio and a filter temperature of -21°C to make a dewaxed oil having the properties shown in Table 8.

TABLE 7

Process ConditionsR1 Conditions

Pressure, psig	1800 (12.4 mPa)
TGR, scf/B	2500 (445 m ³ /m ³)
Space Velocity, v/v/h	0.7
Temperature, °C	375

R2 Conditions

Pressure, psig	1800
TGR, scf/B	2400 (427 m ³ /m ³)
Space Velocity, v/v/h	2.5
Temperature, °C	290

TABLE 8

Product Properties

Viscosity, cSt at 100°C,	4.182
Viscosity, cSt at 40°C,	20.495
SUS, cP at 100°F	107.7
VI	106
Pour Point, °C	-19
Brookfield Viscosity, at -40°C	39900

This dewaxed oil was then catalytically dewaxed over a 0.5 wt% Pt TON (zeolite)/Pt Silica-alumina (25:75 wt/wt, zeolite:silica-alumina) mixed powder composite catalyst under the conditions shown in Table 9 and to produce the products, after fractionation at 370°C, shown in Table 9.

TABLE 9

<u>Process Conditions</u>		
Pressure, psig	1000	1000
TGR, scf/B	2500	2500
Space Velocity, v/v/h	1.0	1.0
Temperature, °C	295	303
Yield, wt%	67	60
<u>Product Properties</u>		
Viscosity, cSt at 100°C,	4.150	4.122
Viscosity, cSt at 40°C,	20.634	20.441
SUS, cP at 100°F	108.4	107.5
VI	101.7	101.3
Pour Point, °C	-33	-40
Brookfield Viscosity, cP at -40°C	32100	22900

The dewaxed oils, both feed and products from the catalytic dewaxer were formulated as Automatic Transmission Fluids using a Ford type ATF ad pack (22 wt% treat rate of ATF ad pack, 78 wt% dewaxed oil) and Brookfield Viscosities at -40°C measured. The Brookfield Viscosities for both feed and products are shown in Tables 8 and 9 respectively.

EXAMPLE 10

This example illustrates the advantage of catalytic dewaxing a total liquid product produced from hydrotreating a raffinate over the process described in Example 9. Catalytic dewaxing is shown to give a product with improved VI over that obtained by solvent dewaxing at the same pour points. In addition, the catalytic dewaxed products have much better low temperature properties (as defined by lower Brookfield Viscosity) than the corresponding solvent dewaxed product.

A hydrotreated raffinate product was made under the conditions listed in Table 10.

TABLE 10

Process ConditionsR1 Conditions

Pressure, psig	1800 (12.4 mPa)
TGR, scf/B	2400 (427 m ³ /m ³)
Space Velocity, v/v/h	0.7
Temperature, °C	382

R2 Conditions

Pressure, psig	1800
TGR, scf/B	2400
Space Velocity, v/v/h	2.5
Temperature, °C	290

The hydrotreated raffinate total liquid product made under the conditions in Table 10 was topped at 370°C to give a 370°C+ product which was solvent dewaxed using MIBK in a 3:1 solvent to raffinate product ratio and a filter temperature of -21°C to make a dewaxed oil having the properties shown in Table 11.

TABLE 11

Product Properties

Viscosity, cSt at 100°C,	3.824
Viscosity, cSt at 40°C,	17.5
SUS, cP at 100°F	93.5
VI	109.3
Pour Point, °C	-19
Yield on TLP, wt%	65.5
Brookfield Viscosity, cP at -40°C	26800

The total liquid product from this step was then catalytically dewaxed over a 0.5 wt% Pt TON (zeolite)/Pt Silica-alumina (25:75 wt/wt, zeolite:silica-alumina) mixed powder composite catalyst under the conditions shown in Table 12 and to produce the products, after topping at 370°C, shown in Table 11.

TABLE 12

<u>Process Conditions</u>			
Pressure, psig	1000	1000	1000 (7.0 mPa)
TGR, scf/B	2500	2500	2500 (445m ³ /m ³)
Space Velocity, v/v/h	1.0	1.0	1.0
Temperature, °C	304	306	314
Yield, wt%	48.2	46.3	33.5
<u>Product Properties</u>			
Viscosity, cSt at 100°C	3.721	3.672	3.593
Viscosity, cSt at 40°C	16.511	16.256	15.925
SUS, cP at 100°F	89.0	87.8	86.4
VI	112.6	111	107.0
Pour Point, °C	-20	-23	-39
Brookfield Viscosity, at -40°C	13640	12740	10600

The dewaxed oils, both solvent dewaxed and the products from the catalytic dewaxer, were formulated as Automatic Transmission Fluids using a Ford type ATF ad pack (22 wt% treat rate of ATF ad pack, 78 wt% dewaxed oil) and Brookfield Viscosities at -40°C measured. The Brookfield Viscosities for both feed and products are shown in Tables 5 and 6 respectively.

Figure 9 shows the benefit of catalytic dewaxing both the DWO and total liquid products. Comparing the data in Examples 9 and 11 (Tables 9 and 12) shows a further benefit for dewaxing a TLP vs. a DWO in that the former results in products having a higher VI at the same pour point. Catalytic dewaxing also

improves the VI of the products from dewaxing a TLP over that obtained by solvent dewaxing.

EXAMPLE 11

This example further illustrates the advantage of catalytic dewaxing a total liquid product versus solvent dewaxing to the same pour point. Catalytic dewaxing is shown to give a product with improved VI over that obtained by solvent dewaxing at the same pour points. In addition, the catalytic dewaxed products have much better low temperature properties (as defined by lower Brookfield Viscosity) than the corresponding solvent dewaxed product.

A hydrotreated raffinate product was made under the conditions listed in Table 10.

TABLE 13

Process Conditions

R1 Conditions

Pressure, psig	1800 (12.5 mPa)
TGR, scf/B	2400 (427 m ³ /m ³)
Space Velocity, v/v/h	0.7
Temperature, °C	382

R2 Conditions

Pressure, psig	1800
TGR, scf/B	2400
Space Velocity, v/v/h	2.5
Temperature, °C	290

The hydrotreated raffinate total liquid product made under the conditions in Table 4 was topped at 370°C to give a 370°C+ product which was solvent

dewaxed using MIBK in a 3:1 solvent to raffinate product ratio and a filter temperature of -21°C to make a dewaxed oil having the properties shown in Table 14.

TABLE 14

<u>Product Properties</u>	
Viscosity, cSt at 100°C,	5.811
Viscosity, cSt at 40°C,	34.383
SUS, cP at 100°F	177
VI	110.6
Pour Point, °C	-21
Yield on TLP, wt%	64.6
Brookfield Viscosity, cP at -40°C	148200

The total liquid product from this step was then catalytically dewaxed over a 0.5 wt% Pt TON (zeolite) / Pt Silica-alumina (25:75 wt/wt, zeolite: silica-alumina) mixed powder composite catalyst under the conditions shown in Table 15 and to produce the products , after topping at 370°C, shown in Table 11.

TABLE 15

<u>Process Conditions</u>			
Pressure, psig	1000	1000	1000
TGR, scf/B	2500	2500	2500
Space Velocity, v/v/h	1.0	1.0	1.00
Temperature, °C	304	306	314
Yield, wt%	48.2	46.3	33.5
<u>Product Properties</u>			
Viscosity, cSt at 100°C,	5.309	5.261	5.115
Viscosity, cSt at 40°C,	28.899	28.552	27.364
SUS, cP at 100°F	148.9	147.2	141.2
VI	117.6	117.0	116.4
Pour Point, °C	-13	-20	-18
Brookfield Viscosity, at -40°C	47150	35650	38150

The dewaxed oils, both solvent dewaxed and the products from the catalytic dewaxer, were formulated as Automatic Transmission Fluids using a Ford type ATF ad pack (22 wt% treat rate of ATF ad pack, 78 wt% dewaxed oil) and Brookfield Viscosities at -40°C measured. The Brookfield Viscosities for both feed and products are shown in Tables 14 and 15 respectively.

Figure 10 is a graphical illustration of the results from Example 11. This example also illustrates the benefit of catalytic dewaxing versus solvent dewaxing in that the VI of the products from catalytic dewaxing are higher than that obtained by solvent dewaxing.

CLAIMS:

1. A process for producing a lubricating oil basestock meeting at least 90 wt% saturates by selectively hydroconverting a raffinate produced from solvent refining a lubricating oil feedstock which comprises:

- (a) conducting the lubricating oil feedstock to a solvent extraction zone and separating therefrom an aromatics rich extract and a paraffins rich raffinate;
- (b) stripping the raffinate of solvent to produce a raffinate feed having a dewaxed oil viscosity index from about 85 to about 105 and a final boiling point of no greater than about 650°C;
- (c) passing at least a portion of the raffinate feed to a first hydroconversion zone and processing the raffinate feed in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 420°C, a hydrogen partial pressure of from 1000 to 2500 psig, space velocity of 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a first hydroconverted raffinate;
- (d) passing the hydroconverted raffinate from the first hydroconversion zone to a second hydroconversion zone and processing the hydroconverted raffinate in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 400°C provided that the temperature in second hydroconversion is not greater than the temperature in the first hydroconversion zone, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a second hydroconverted raffinate;

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- (e) passing the second hydroconverted raffinate to a hydrofinishing zone and conducting cold hydrofinishing of the second hydroconverted raffinate in the presence of a hydrofinishing catalyst at a temperature of from 260 to 360°C, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 5 LHSV and a hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a hydrofinished raffinate;
- (f) passing the hydrofinished raffinate to a separation zone to remove products having a boiling less than about 250°C; and
- (g) passing the hydrofinished raffinate from step (f) to a dewaxing zone and catalytically dewaxing the hydrofinished raffinate under catalytic dewaxing conditions in the presence of hydrogen and a catalytic dewaxing catalyst comprising a metal hydrogenation component and a crystalline 10 or 12 ring molecular sieve.

2. A process for selectively hydroconverting a raffinate produced from solvent refining a lubricating oil feedstock which comprises:

- (a) conducting the lubricating oil feedstock to a solvent extraction zone and separating therefrom an aromatics rich extract and a paraffins rich raffinate;
- (b) stripping the raffinate of solvent to produce a raffinate feed having a dewaxed oil viscosity index from about 85 to about 105 and a final boiling point of no greater than about 650°C;
- (c) passing at least a portion of the raffinate feed to a first hydroconversion zone and processing the raffinate feed in the presence of a non-acidic hydro-conversion catalyst at a temperature of from 340 to 420°C, a hydrogen partial pressure of from 1000 to 2500 psig, space velocity of 0.2 to 3.0 LHSV and a

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hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a first hydroconverted raffinate;

- (d) passing the hydroconverted raffinate from the first hydroconversion zone to a second hydroconversion zone and processing the hydroconverted raffinate in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 400°C provided that the temperature in the second hydroconversion is not greater than the temperature in the first hydroconversion zone, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a second hydroconverted raffinate;
- (e) passing the second hydroconverted raffinate to a hydrofinishing reaction zone and conducting cold hydrofinishing of the second hydroconverted raffinate in the presence of a hydrofinishing catalyst at a temperature of from 260 to 360°C, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 5 LHSV and hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a hydrofinished raffinate;
- (f) solvent dewaxing the hydrofinished raffinate under solvent dewaxing conditions to obtain a dewaxed oil having a pour point less than about 10°C; and
- (g) catalytically dewaxing the solvent dewaxed oil under catalytic dewaxing conditions in the presence of hydrogen and a catalytic dewaxing catalyst comprising a metal hydrogenation component and a crystalline 10 or 12 ring molecular sieve to produce a dewaxed lubricating oil basestock.

3. A process for producing a lubricating oil basestock meeting at least 90 wt% saturates by selectively hydroconverting a raffinate produced from solvent refining a lubricating oil feedstock which comprises:

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- (a) conducting the lubricating oil feedstock to a solvent extraction zone and separating therefrom an aromatics rich extract and a paraffins rich raffinate;
- (b) stripping the raffinate of solvent to produce a raffinate feed having a dewaxed oil viscosity index from about 85 to about 105 and a final boiling point of no greater than about 650°C;
- (c) passing at least a portion of the raffinate feed to a first hydroconversion zone and processing the raffinate feed in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 420°C, a hydrogen partial pressure of from 1000 to 2500 psig, space velocity of 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a first hydroconverted raffinate;
- (d) passing the hydroconverted raffinate from the first hydroconversion zone to a second hydroconversion zone and processing the hydroconverted raffinate in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 400°C provided that the temperature in second hydroconversion is not greater than the temperature in the first hydroconversion zone, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 Scf/B to produce a second hydroconverted raffinate;
- (e) passing the second hydroconverted raffinate to a separation zone to remove products having a boiling less than about 250°C;

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- (f) passing the hydroconverted raffinate from step (e) to a dewaxing zone and catalytically dewaxing the hydroconverted raffinate under catalytic dewaxing conditions in the presence of hydrogen and a catalytic dewaxing catalyst comprising a metal hydrogenation component and a crystalline 10 or 12 ring molecular sieve to yield a dewaxed hydroconverted raffinate; and
- (g) passing the dewaxed hydroconverted raffinate to a hydrofinishing zone and conducting cold hydrofinishing of the dewaxed hydroconverted raffinate in the presence of a hydrofinishing catalyst at a temperature of from 260 to 360°C, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 5 LHSV and a hydrogen to feed ratio of from 500 to 5000 scf/B to produce a lubricating oil basestock.

4. A process for selectively hydroconverting a raffinate produced from solvent refining a lubricating oil feedstock which comprises:

- (a) conducting the lubricating oil feedstock to a solvent extraction zone and separating therefrom an aromatics rich extract and a paraffins rich raffinate;
- (b) stripping the raffinate of solvent to produce a raffinate feed having a dewaxed oil viscosity index from about 85 to about 105 and a final boiling point of no greater than about 650°C;
- (c) passing at least a portion of the raffinate feed to a first hydroconversion zone and processing the raffinate feed in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 420°C, a hydrogen partial pressure of from 1000 to 2500 psig, space velocity of 0.2 to 3.0 LHSV and a

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hydrogen to feed ratio of from 500 to 5000 scf/B to produce a first hydroconverted raffinate;

- (d) passing the hydroconverted raffinate from the first hydroconversion zone to a second hydroconversion zone and processing the hydroconverted raffinate in the presence of a non-acidic hydroconversion catalyst at a temperature of from 340 to 400°C provided that the temperature in the second hydroconversion is not greater than the temperature in the first hydroconversion zone, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 3.0 LHSV and a hydrogen to feed ratio of from 500 to 5000 scf/B to produce a second hydroconverted raffinate;
- (e) solvent dewaxing the second hydroconverted raffinate under solvent dewaxing conditions to obtain a dewaxed oil having a pour point less than about 10°C;
- (f) catalytically dewaxing the solvent dewaxed oil under catalytic dewaxing conditions in the presence of hydrogen and a catalytic dewaxing catalyst comprising a metal hydrogenation component and a crystalline 10 or 12 ring molecular sieve to produce a catalytically dewaxed oil; and
- (g) passing the catalytically dewaxed oil to a hydrofinishing reaction zone and conducting cold hydrofinishing of the catalytically dewaxed oil in the presence of a hydrofinishing catalyst at a temperature of from 260 to 360°C, a hydrogen partial pressure of from 1000 to 2500 psig, a space velocity of from 0.2 to 5 LHSV and hydrogen to feed ratio of from 500 to 5000 scf/B to produce a dewaxed lubricating oil basestock.

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5. The process of claims 1 or 2 wherein there is no disengagement between the first hydroconversion zone, the second hydroconversion zone and the hydrofinishing reaction zone.

6. The process of claims 1, 2, 3 or 4 wherein the non-acidic hydroconversion catalyst is cobalt/molybdenum, nickel/molybdenum or nickel/tungsten on alumina.

7. The process of claims 1, 2, 3 or 4 wherein the hydrogen partial pressure in the first hydroconversion zone, the second conversion zone or the hydrofinishing zone is from 1000 to 2000 psig (7.0 to 12.5 mPa).

8. The process of claims 1, 2, 3 or 4 wherein the non-acidic hydroconversion catalyst has an acidity less than about 0.5, said acidity being determined by the ability of the catalyst to convert 2-methyl-2-pentene to 3-methyl-2-pentene and 4-methyl-2-pentene and is expressed as the mole ratio of 3-methyl-2-pentene to 4-methyl-2-pentene.

9. The process of claims 1, 2, 3 or 4 wherein the catalytic dewaxing catalyst is a zeolite selected from ZSM-5, ZSM-11, ZSM-12, theta-1, ZSM-23, ZSM-35, ferrierite, ZSM-48, ZSM-57, beta, mordenite and offretite.

10. The process of claims 1, 2, 3 or 4 wherein the catalytic dewaxing catalyst is an aluminum phosphate selected from SAPO-11, SAPO-31 and SAPO-41.

11. The process of claims 1, 2, 3 or 4 wherein the catalytic dewaxing catalyst is a composite of a crystalline molecular sieve and an amorphous component.

12. The process of claims 1, 2, 3 or 4 wherein the catalytic dewaxing catalyst is layered catalyst containing a first layer of amorphous component and a second layer of crystalline molecular sieve.
13. The process of claims 1, 2, 3 or 4 wherein the metal hydrogenation component of the catalytic dewaxing catalyst is at least one of a Group VI and Group VIII metal.
14. The process of claims 1 or 2 wherein the catalytic dewaxing step is followed by a cold hydrofinishing step.
15. The process of claim 11 wherein the amorphous component of the dewaxing catalyst is selected from silica-alumina, silica magnesia, halogenated alumina, yttria silica-alumina and mixtures thereof.
16. The process of claim 13 wherein the metal hydrogenation component is at least one of Pt or Pd.
17. The process of claims 2 or 4 wherein solvent dewaxing comprises mixing the hydrofinished raffinate with a chilled solvent to form an oil-solvent solution mixed with precipitated wax, separating precipitated wax from the oil-solvent solution, and separating the solvent from the solvent-oil solution thereby forming a solvent dewaxed oil.
18. The process of claim 17 wherein the solvent is at least one of propane, butane, methyl ethyl ketone, methyl isobutyl ketone, benzene, toluene and xylene.

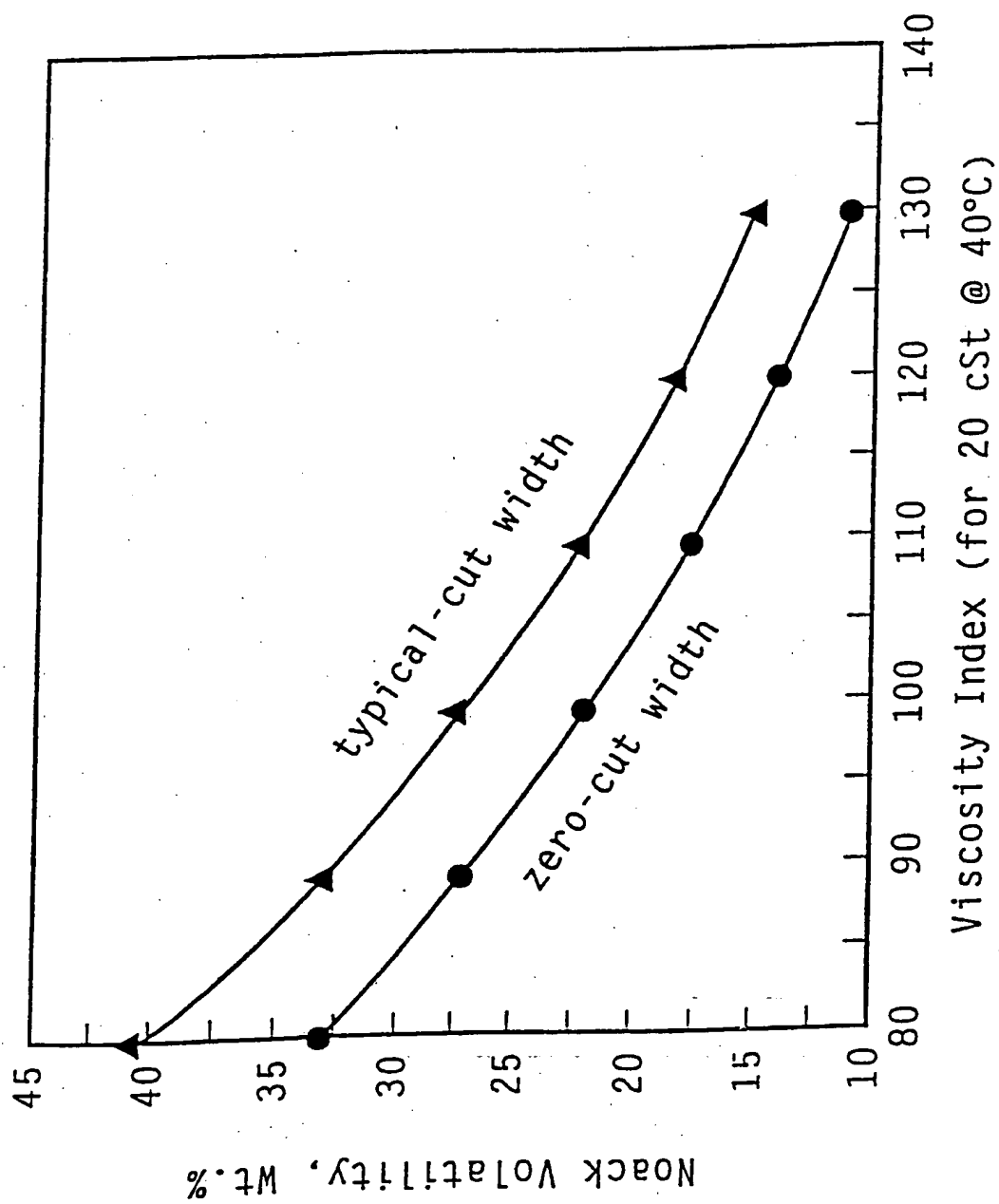


FIG. 1

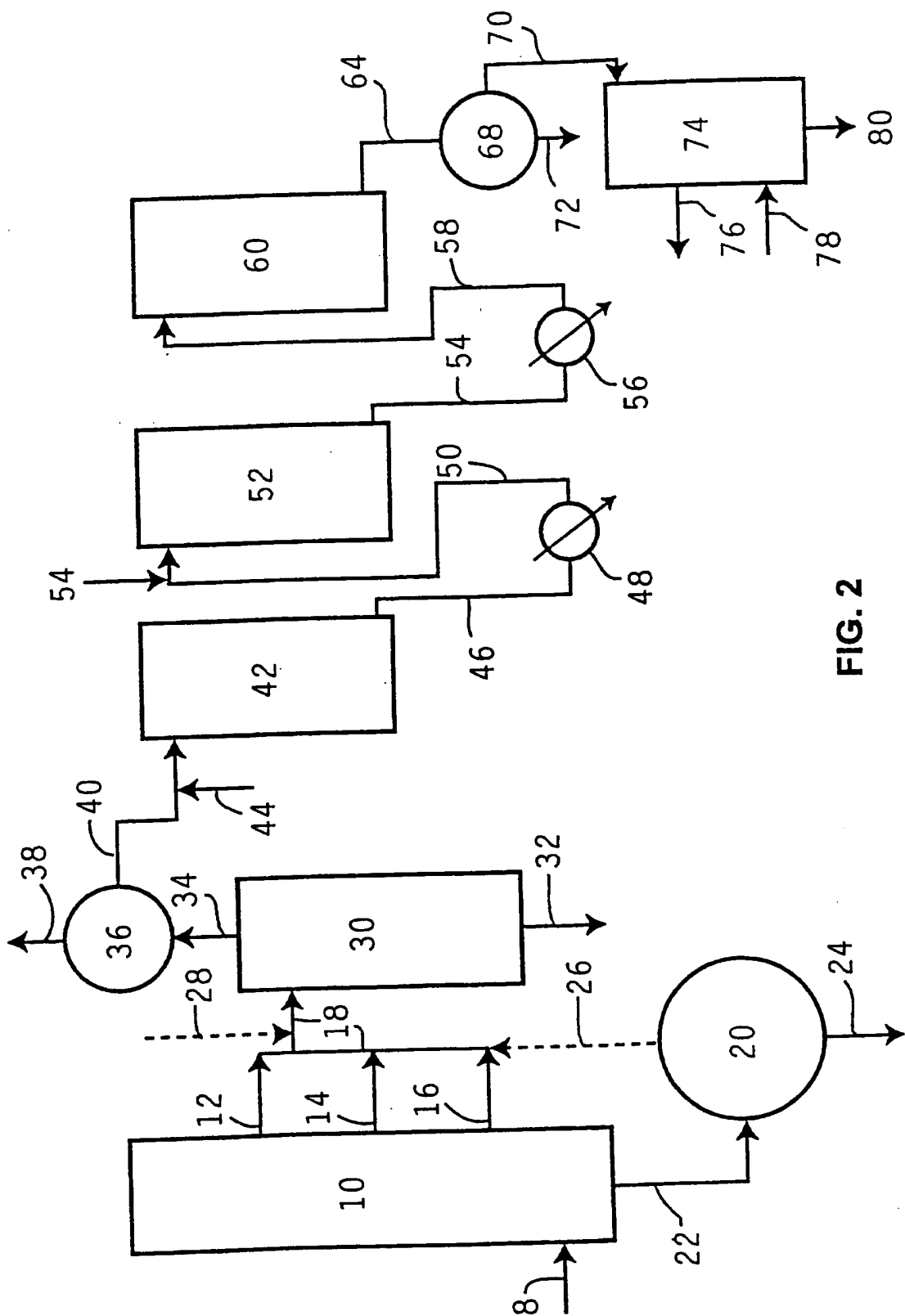


FIG. 2

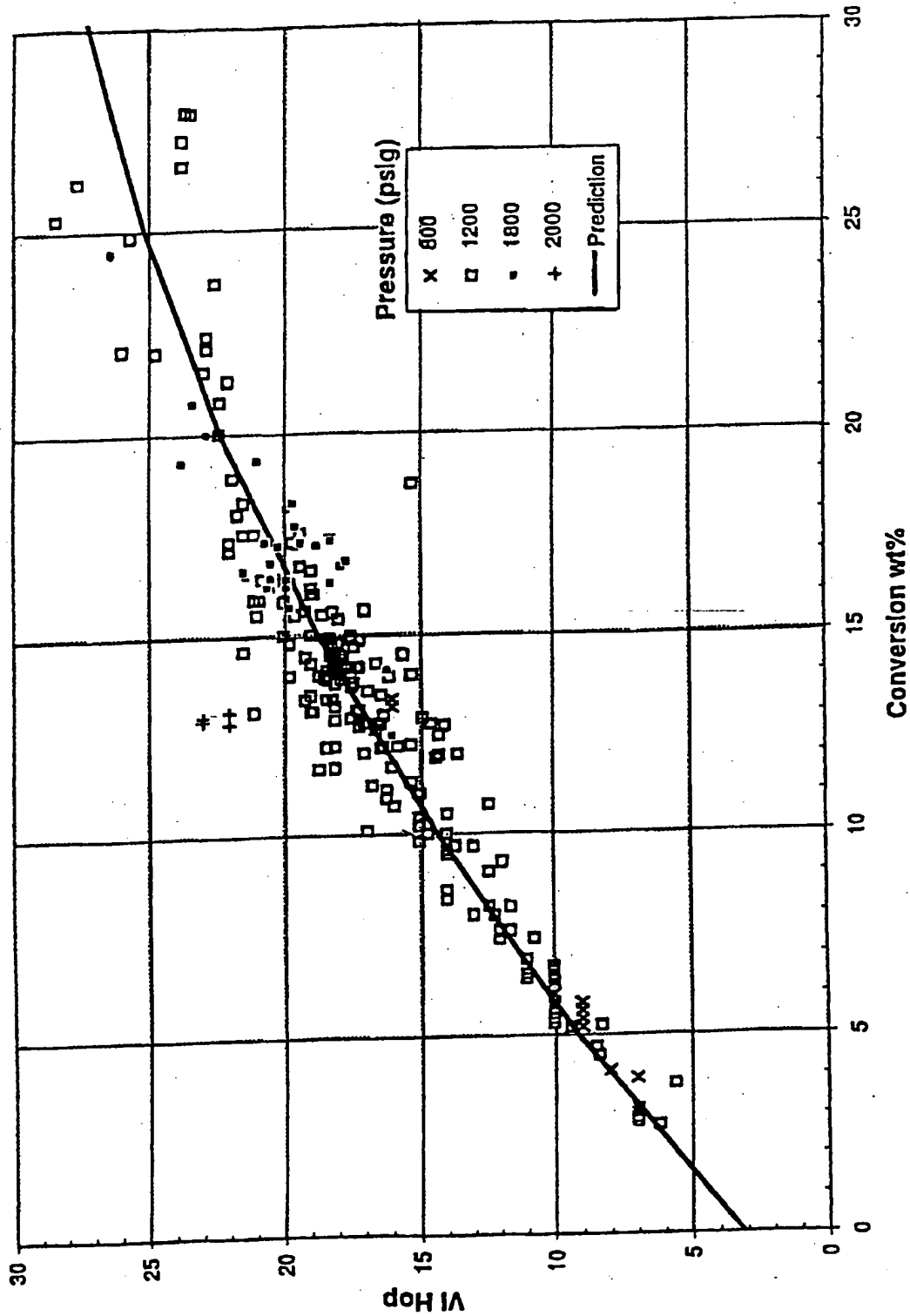


FIG. 3

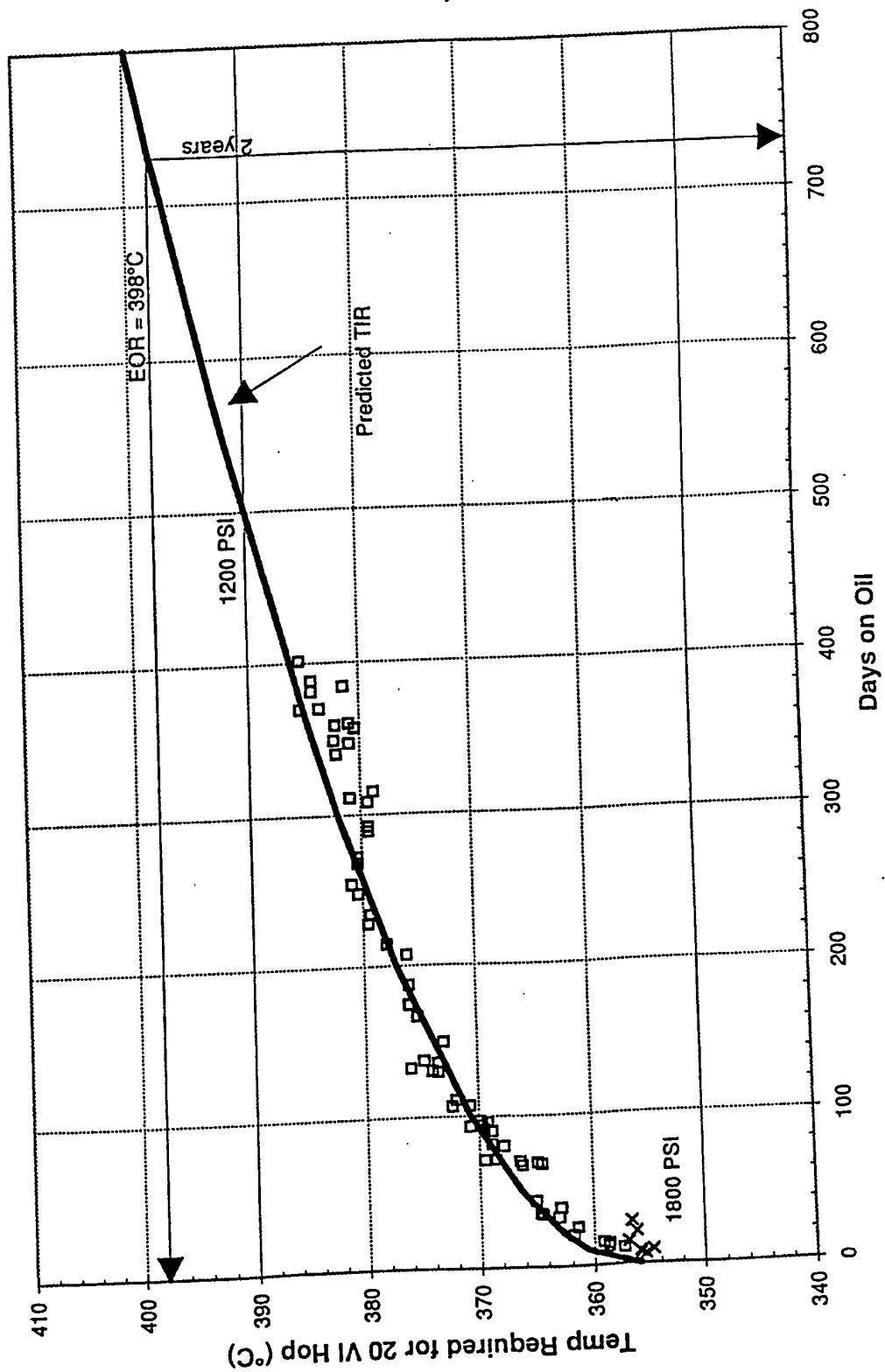


FIG. 4

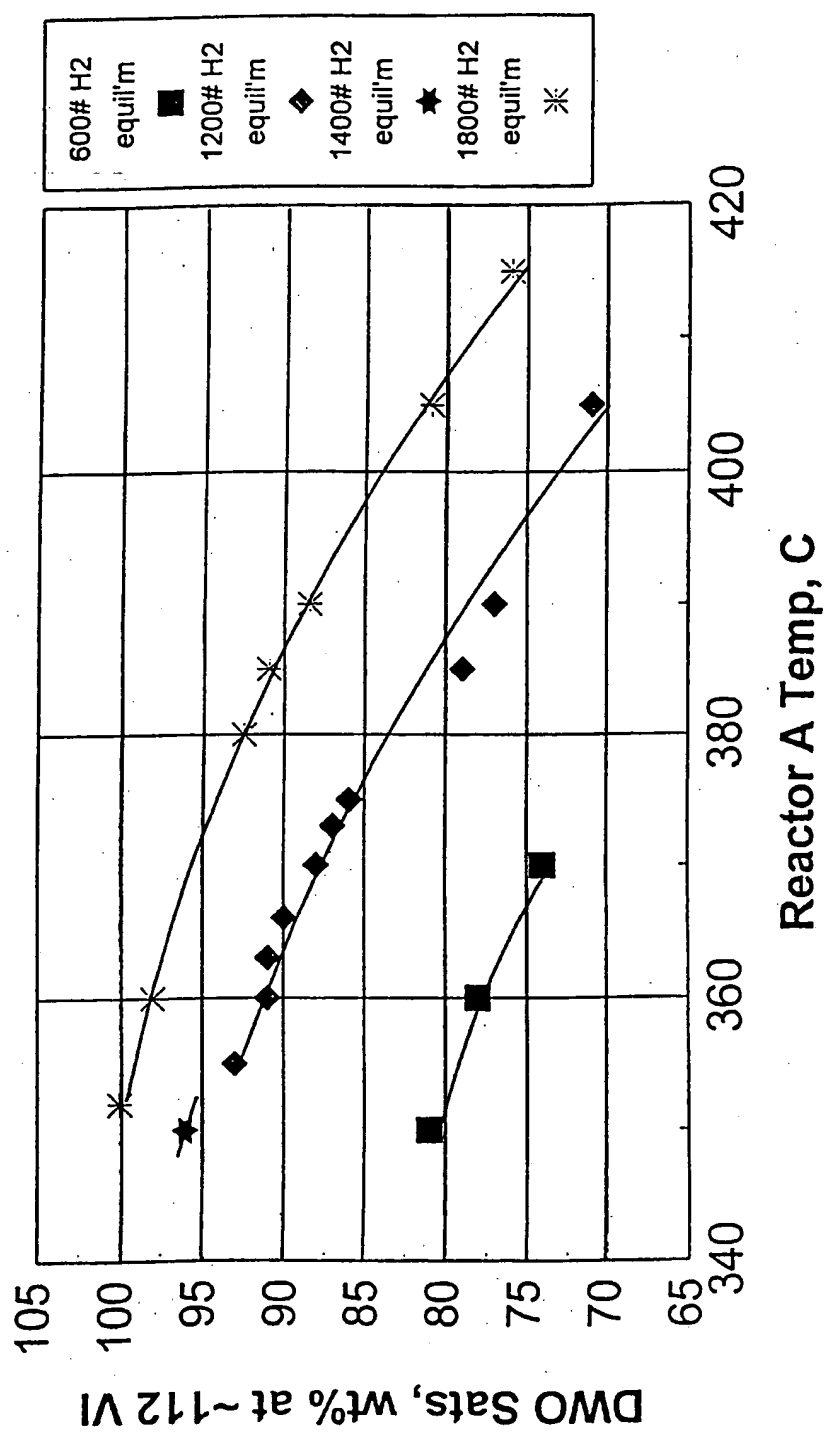


FIG. 5

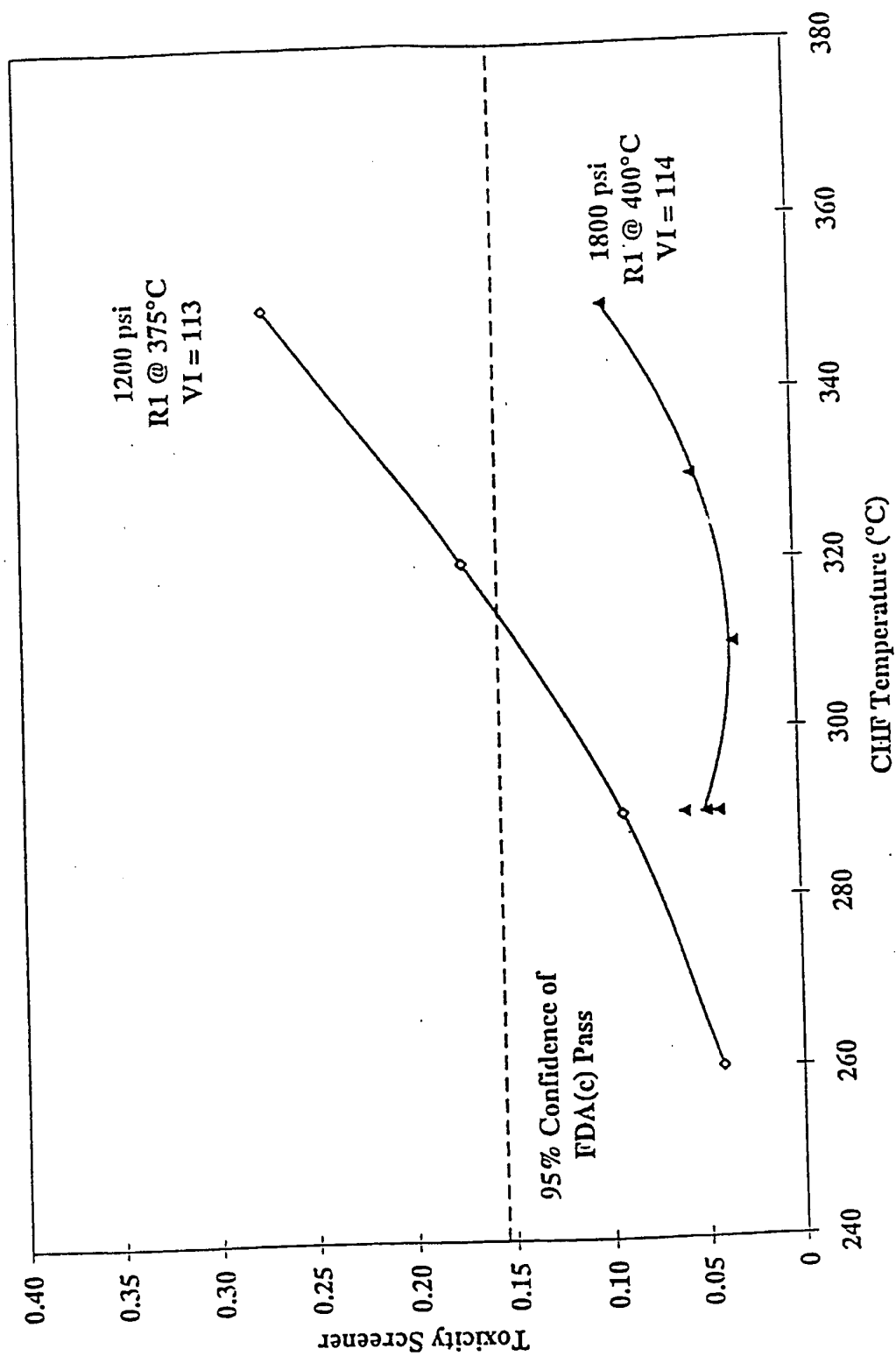
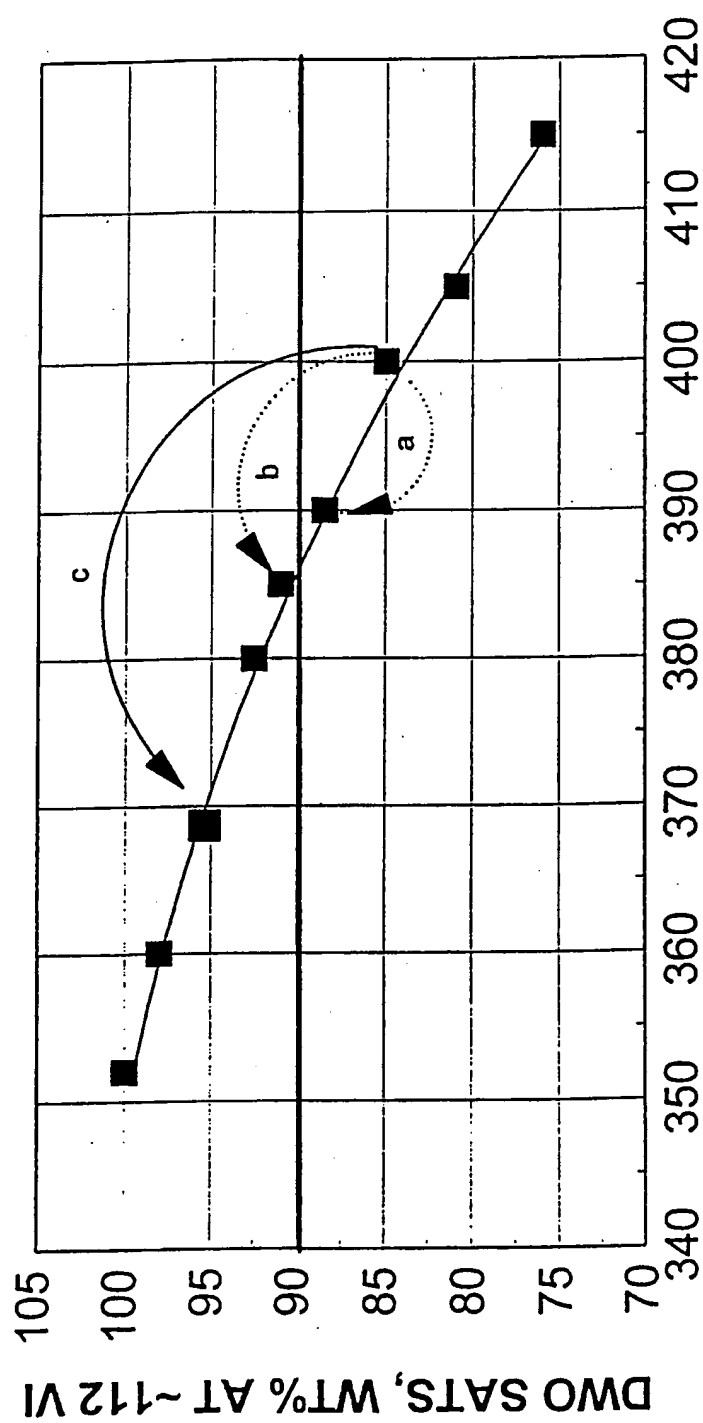


FIG. 6



Reactor A+B TEMP, C

Reactor C Conditions: (a) 330C, 2.5 LHSV, 1800# H2; (b) 350C, 2.5 LHSV, 1800# H2
(c) 350, 1 LHSV, 1800# H2

FIG. 7

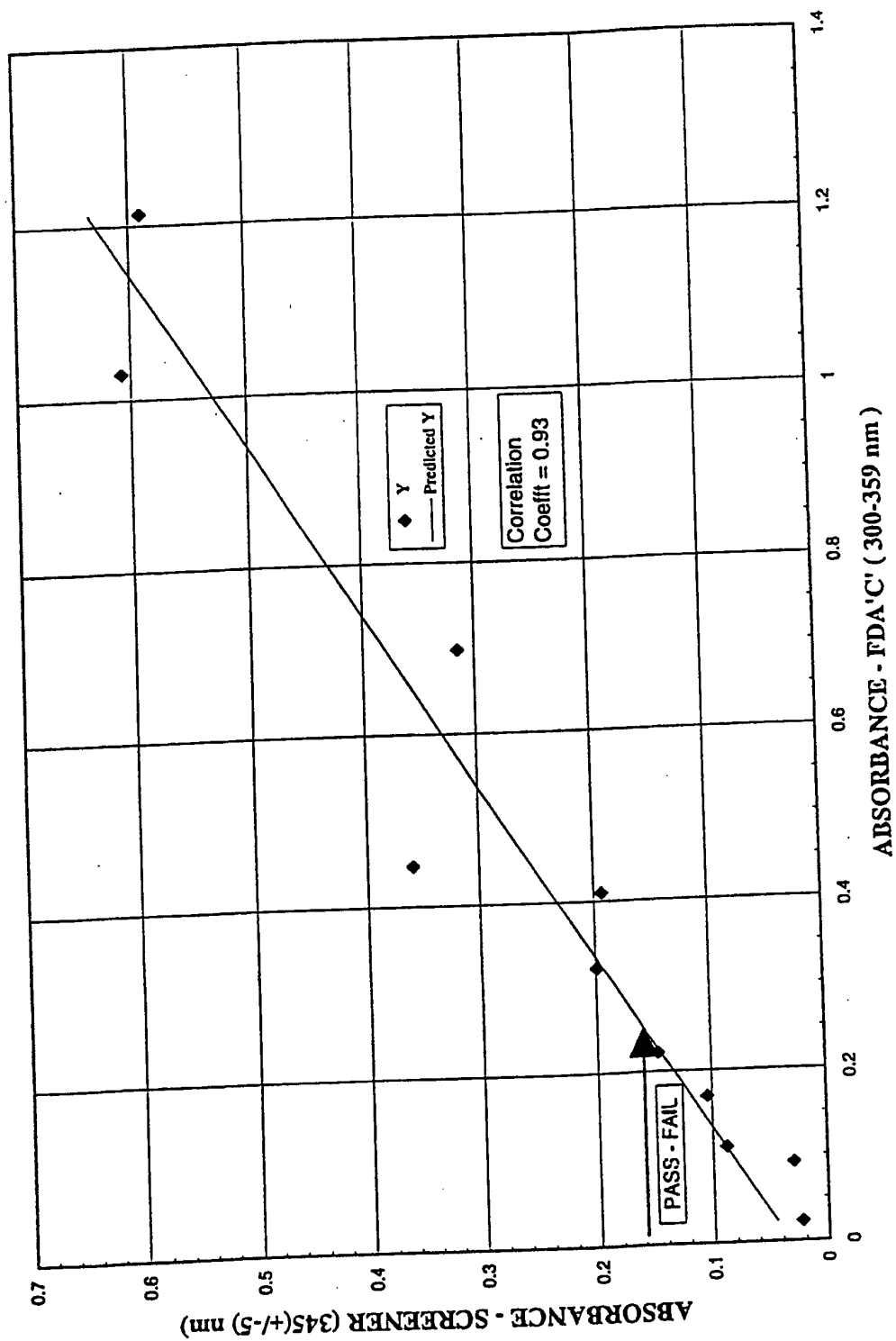


FIG. 8

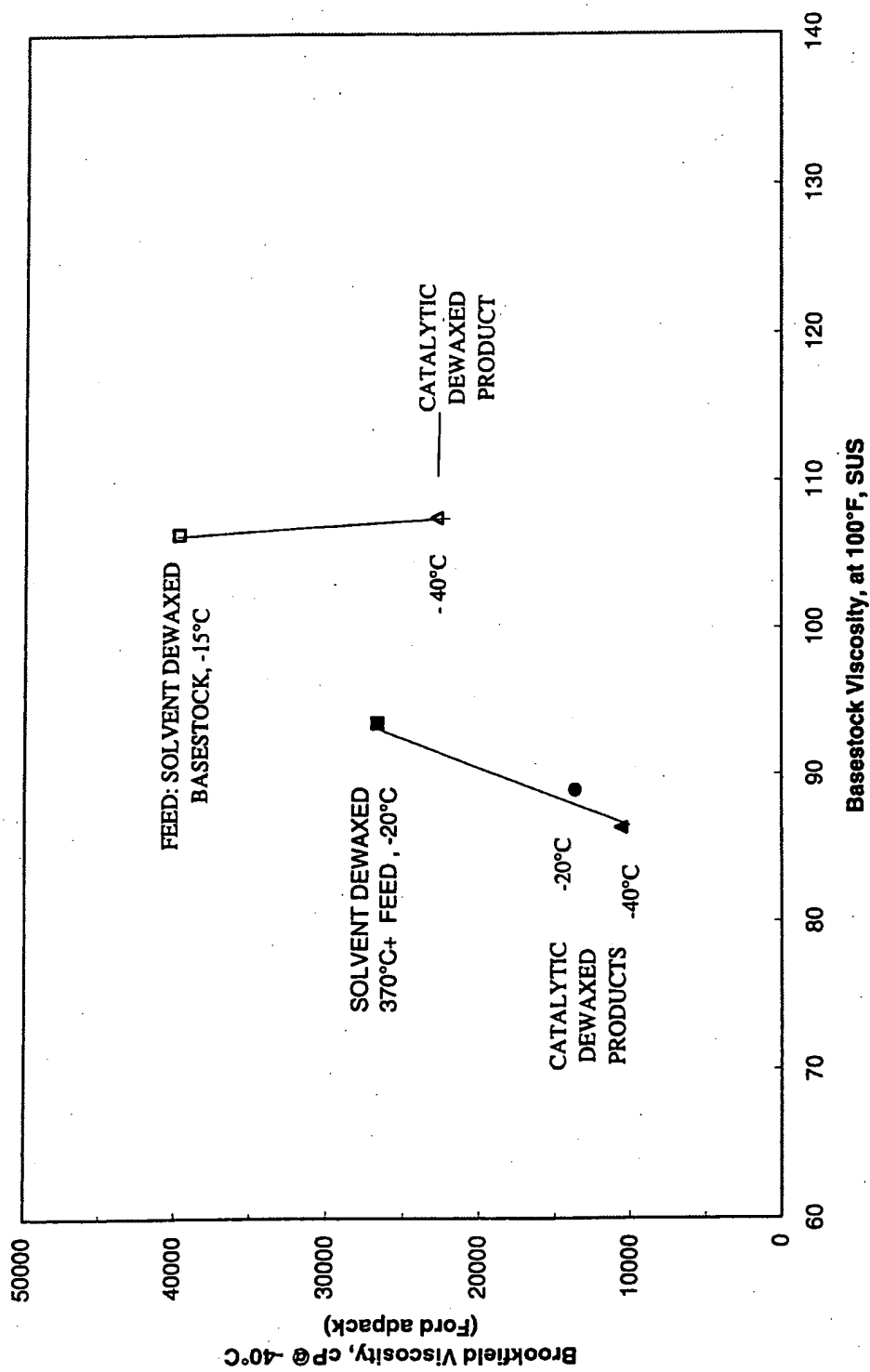


FIGURE 2

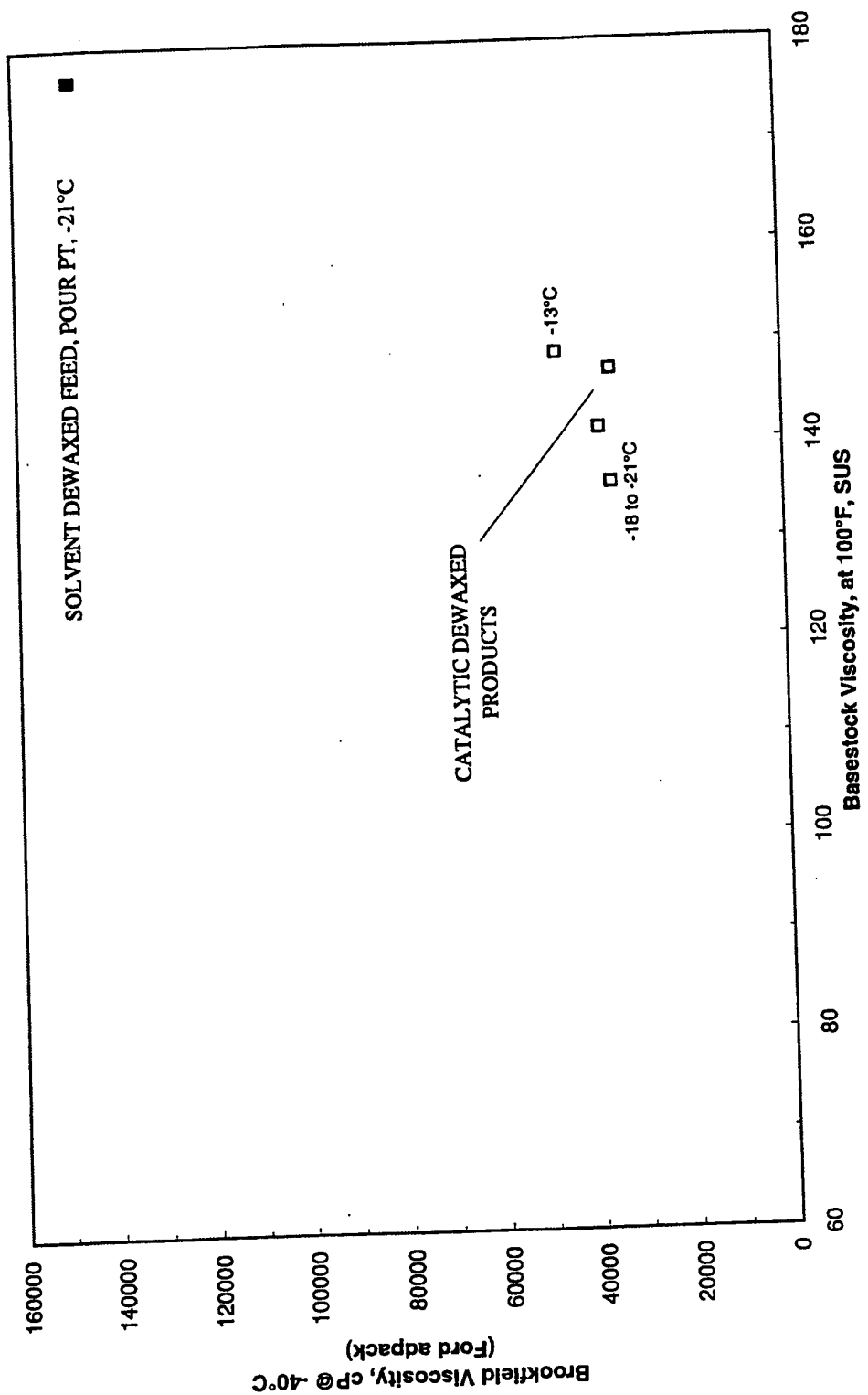


FIGURE 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/03108

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10G 1/04

US CL : 208/27, 59, 60, 97, 311

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/27, 59, 60, 97, 311

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,300,213 A (BARTILUCCI et al) 05 April 1994, col 4, lines 1-67.	1-18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

31 MARCH 1999

Date of mailing of the international search report

06 MAY 1999

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